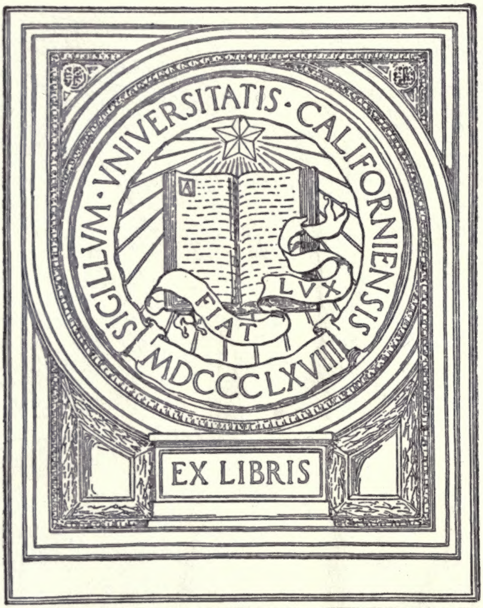
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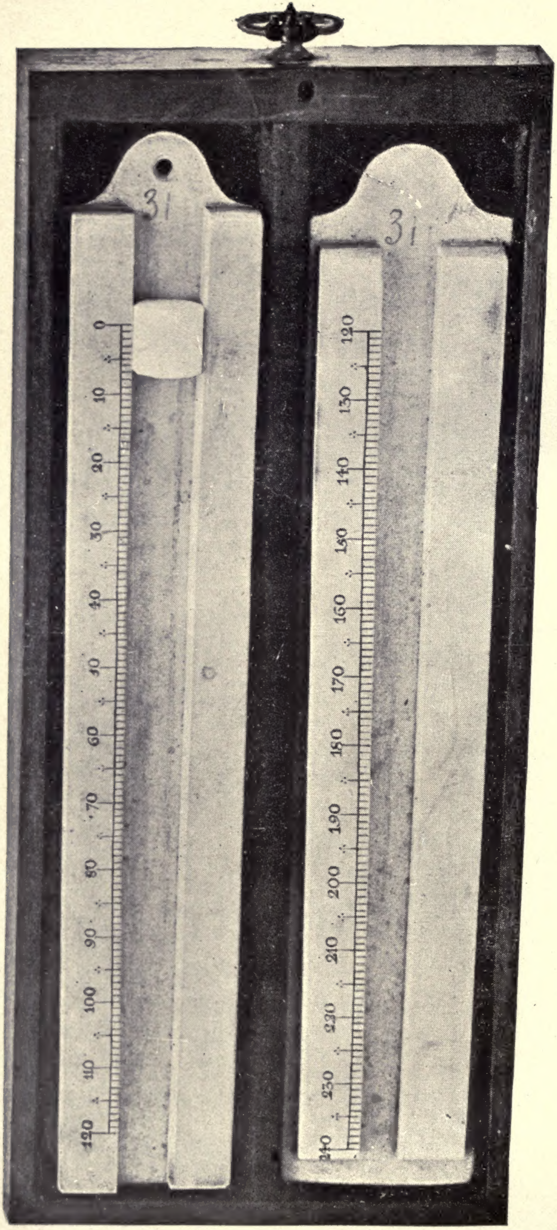

Wedgwood's Pyroscope. *Frontispiece.*

UNIV. OF
CALIFORNIA

The Measurement of High Temperatures

BY

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BUREAU OF STANDARDS

AND

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PREFACE I.

THE main purpose of this preface is to recall the origin of the volume Mr. Burgess and I present to the reader. For a long time, all precise, scientific investigations at high temperatures were made impossible by the absence of suitable methods for the measurement of these temperatures. Wedgwood, more than a century ago, had already insisted on the capital importance of the carrying out of high-temperature investigations, and devised for this purpose his pyrometer, which is but an arbitrary-comparison apparatus. The question was taken up later by many scientists, but with little success, until I called attention definitely to the precision to be obtained by the judicious use of thermoelectric couples.

Pouillet about 1830, and afterwards Edmond Becquerel, had made some measurements with the gas thermometer provided with a platinum bulb. This method, however, was completely discredited following the discovery, by Henry Sainte-Claire Deville, of the permeability of platinum to hydrogen; and it is only since the very recent employment of platinum-wound electric resistance furnaces, free from all combustible material, that it has been possible to obtain accurate measurements with the platinum-bulb gas thermometer; but its complexity and the difficulty of manipulation limit its use to the standardization of other measuring apparatus.

Henry Becquerel, later his son Edmond, and also Pouillet, advocated the employment of thermoelectric couples; but their use did not spread, and Regnault emphatically condemned them after finding serious irregularities in their behavior. These anomalies, the cause of which he did not then recognize, were due, as I showed later, to the use of iron as one of the

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metals of the couple, and to imperfections in the methods of electrical measurements.

Violle, following Regnault and Sir William Siemens, proposed the calorimetric method with platinum as the heated substance, instead of iron used by Regnault and copper by Siemens, in their industrial pyrometers. This complicated method, of delicate and slow manipulation, did not come into general use.

Mention should also be made of other isolated and even more restricted attempts, the application of which hardly exceeded a series of observations by a single experimenter. Sir William Siemens proposed the electrical resistance pyrometer; before this, Edmond Becquerel had suggested a radiation pyrometer; finally, several observers sought to apply to determinations of the sun's temperature certain heat-radiation methods.

In 1885, when I attacked the problem of the measurement of high temperatures, it is fair to say there existed nothing definite available on this important question; we possessed only qualitative observations for temperatures above 500° C. Engaged at that time in industrial studies relative to the manufacture of cement, I sought a method which above all would be rapid and simple, and decided on the use of thermoelectric couples, intending to determine the order of magnitude of the sources of error noticed by Regnault. The readings of even a crude galvanometer might be very useful in technical work, provided the limitations of its accuracy were appreciated. I soon recognized that the errors attributed to this method could easily be eliminated by discarding in the construction of the couples certain metals, such as iron, nickel, and palladium, which give rise to singular anomalies; and indicated a simple test for recognizing the suitable metals. One takes a stretched wire of the metal, the ends of which are connected to the terminals of a sufficiently sensitive galvanometer, indicating at least $\frac{1}{10000}$ volt, and the wire is then heated from point to point with a Bunsen flame, which is carried back and forth beneath the wire, when no electric currents should be produced. Now, iron and palladium, the two metals advocated by Becquerel and Pouillet, give rise to large and variable parasite currents which diminish the accuracy of the measurements. Among the different metals and alloys studied, pure platinum and the alloy of platinum and rhodium which are still used to-day, gave the most satisfactory results.

Finally, I called attention to the importance, overlooked by Regnault, of employing only galvanometers of high resistance, to avoid the influence of variations in resistance of the wires of the couple when heated. I recommended also the calibration of the couples, not against the air thermometer directly, as Becquerel had tried to do, but in terms of the fixed points of boiling or fusion of certain pure substances, in such a way that, when these temperatures should be known more exactly, as is the case since my earlier researches, the results could be corrected with certainty.

Some months later, at the request of Sir Robert Hadfield, director of the Hecla Steel Works, I developed an optical pyrometer, and calibrated it by comparison with the thermoelectric couple. By means of these two instruments, I determined a large number of temperatures, in the laboratory and in the industries, and rectified, often by several hundred degrees, the numbers previously admitted in terms of fantastic estimations.

From this date, the measurement of high temperatures came rapidly into general use in the laboratory as well as in the industries. A few years later, in a course of lectures delivered during the year 1898 at the Collège de France, I thought it useful to give a summary of the progress accomplished. These lectures, gathered into book form with the aid of my assistant, Mr. Boudouard, formed the first edition of this work. Mr. Burgess, who had followed my lectures, took the trouble to translate it into English; but, while there was little demand for the French edition, the English translation was soon exhausted. Mr. Burgess wrote a second edition, considerably improved and enlarged by him; this is again exhausted. This time Mr. Burgess has rewritten anew the whole book, so that it is no longer a translation but an original work which we present to the reader.

For several years past, my studies have taken me into other fields of investigation, and I have been unable to follow the considerable progress realized in the measurement of temperatures. Mr. Burgess, on the contrary, has been actively interested in these new researches and to him is due an important part in the more recent advances. Consequently, this book is much more his work than mine, which enables me to praise it as it deserves, and state that this publication will render great service both to investigators and engineers.

H. Le CHATELIER.

Paris, *February 15, 1911.*

PREFACE II.

SINCE the appearance in 1900 of *Mesure des Températures Elevées* by Messrs. Le Chatelier and Boudouard, the theory and practice of pyrometry have grown greatly, and methods which at that time were in a tentative stage of development have been improved in accuracy and convenience, and adapted by means of new instruments both to technical and scientific requirements.

In gas pyrometry, accurate measurements may be said to have been initiated at the Reichsanstalt by the publication in 1900 of a series of metal freezing points, by Holborn and Day, constituting what is still known as the Reichsanstalt temperature scale.

Again, it is only since 1900 that the significance of the application of the laws of radiation to pyrometry has been appreciated. The theoretical work of Wien, Planck, and others closely contemporaneous with the experimental verifications of Paschen, Lummer and Pringsheim, and many others, was soon followed by the optical and radiation pyrometers of Wanner, Féry, Morse, and Holborn and Kurlbaum, and by many applications to technical and scientific uses.

In thermoelectric and electric resistance pyrometry there has been in recent years an unparalleled improvement in the design of electric measuring instruments, millivoltmeters, potentiometers, galvanometers, Wheatstone bridges and the like, suitable for use in temperature measurements, either in the works or in the laboratory. There have also been executed since 1900 several exact experimental investigations in pyrometry with such apparatus, notably at the several national laboratories and at the Geophysical Laboratory of Washington. Furthermore, the subject of automatic temperature recording has received a great deal of attention, resulting in many new instruments.

In so far as practicable in the following pages, we have dwelt less upon particular types of instrument than on the principles underlying them. We have, however, consulted nearly all the manufacturers of pyrometers as to their practice, and have drawn very freely on the material they have been so kind as to put at our disposal, — material that in several instances is otherwise unpublished, and for which we express our obligation.

We have kept in mind three classes of readers: the student, to whom the historical aspect and fundamental principles are of prime interest; the engineer, who is interested mainly in adapting some method or instrument to his particular technical operation; and the investigator, who has an intensive interest in accurate methods of measurement and their adaptability to his needs. We realize that one book cannot meet satisfactorily all these requirements. If the wants of the investigator have been somewhat neglected, he has ready access to the literature, a summary of which is given in the Bibliography.

We are indebted to Dr. C. W. Waidner for many suggestions; to Dr. R. B. Sosman for reading the chapters on Gas and Thermoelectric Pyrometry; and especially to Dr. A. L. Day, from whose criticisms of the manuscript we have been able to profit greatly.

GEORGE K. BURGESS.

WASHINGTON, *August 24, 1911.*

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HIGH TEMPERATURES

INTRODUCTION.

Wedgwood, the celebrated potter of Staffordshire, the inventor of fine earthenware and of fine china, was the first to occupy himself with the exact estimation of high temperatures. In an article published in 1782, in order to emphasize the importance of this question, he considered at length certain matters a study of which would be well worth while even to-day.

"The greater part of the products obtained by the action of fire have their beauty and their value considerably depreciated by the excess or lack of very small quantities of heat; often the artist can reap no benefit from his own experiments on account of the impossibility to duplicate the degree of heat which he has obtained before his eyes. Still less can he profit from the experiments of others, because it is even less easy to communicate the imperfect idea which each person makes for himself of these degrees of temperature."

Joining example to precept, Wedgwood made for his personal use a pyrometer utilizing the contraction of clay. This instrument, for nearly a century, was the only guide in researches at high temperatures. Replaced to-day by apparatus of a more scientific nature, it has been perhaps too readily forgotten.

Since Wedgwood, many have undertaken the measurement of high temperatures, but with varying success. Too indifferent to practical requirements, the early experimenters above all regarded the problem as a pretext for learned dissertations. The novelty and the originality of methods attracted them more than the precision of the results or the facility of the measurements. Also, up to the past few years, the confusion was on the increase. The temperature of a steel kiln varied according to the different observers from 1500° to 2000°; that of the sun from 1500° to 1,000,000°. More recently there has been great improvement in methods.

First of all, let us point out the chief difficulty of the problem. Temperature is not a measurable quantity in the strict sense of the term. To measure a length or a mass, is to count how many times it is necessary to take a given body chosen as a unit (meter, gram) in order to obtain a complex system equivalent either as to length or mass of the body in question. The possibility of such a measurement presupposes the previous existence of two physical laws: that of equivalence and that of addition. Temperature obeys well the first of these laws; two bodies in temperature equilibrium with a third, and thus equivalent with respect to exchanges of heat in comparison with this third body, will also be equivalent, that is to say, equally in equilibrium with respect to every other body which would be separately in equilibrium with one of them. This law allows determination of temperature by comparison with a substance arbitrarily chosen as a thermometric body. But the second law is wanting; one cannot, by the juxtaposition of several bodies at the same temperature, realize a system equivalent, from the point of view of exchanges of heat, to a body of different temperature; thus temperature is not measured, at least insomuch as one considers only the phenomena of convection.

In order to determine a temperature one observes any phenomenon whatever varying with change of temperature. Thus for the mercury centigrade thermometer the temperature is defined by the *apparent expansion of mercury* from the *point of fusion of ice* measured by means of a unit equal to $\frac{1}{100}$ of the dilatation between the temperature of the *fusion of ice and that of the ebullition of water* under atmospheric pressure.

Thermometric Scales. — For such a determination there are four quantities to be chosen arbitrarily: the *phenomenon* measured, the thermometric *substance*, the *origin* of graduation, and the *unit* of measurement; while in a measurement properly so called there is but one quantity to be arbitrarily chosen, — the magnitude selected as unity. It is evident that the number of thermometric scales may be indefinitely great; too often experimenters have considered it a matter of pride for each to have his own.

Here are some examples of thermometric scales chosen from among many:

Author.	Phenomenon.	Substance.	Origin.	Unit.
Fahrenheit	Dilatation	Mercury	Very cold winter	1/180 ice to B. P.
Réaumur	Dilatation	Mercury	Ice	1/80 ice to B. P.
Celsius	Dilatation	Mercury	Ice	1/100 ice to B. P.
Wedgwood	Permanent contraction	Clay	Dehydrated	1/2400 init. dimens.
Pouillet	Dilat. at const. p.	Air	Ice	1/100 ice to B. P.
(Normal ther.)	Dilat. at const. v.	Hydrogen	Ice	
(Thermodynamic scale)	Reversible heat scale	Anything	Heat = 0	
Siemens	Electric resistance	Platinum	Ice	

The enormous differences above mentioned in the estimations of high temperatures are much more the result of the diversity of the scales than due to the errors of the measurements themselves. Thus the experiments on solar radiation which have led to values varying from 1500° to 1,000,000° are based on measurements which do not differ among themselves by more than 25 per cent.

To escape from this confusion it was first necessary to agree upon a single scale of temperatures; that of the gas thermometer is to-day universally adopted, and this choice may be considered as permanent. The gases possess, more than any other state of matter, a property very important for a thermometric substance, — the possibility of being reproduced at any time and in any place identical with themselves; besides, their dilatation, which defines the scale of temperatures, is sufficient for very precise measurements; finally, this scale is practically identical with the thermodynamic scale. This last is in theory more important than all the other properties because it is independent of the nature of the phenomena and of the substances employed. It gives, too, a veritable measure and not a simple comparison; its only inconvenience is for the moment not to be experimentally realizable, at least rigorously, but this will probably not always be the case.

The adoption of the scale of the gas thermometer does not in any way imply the obligation to use this instrument actually in all measurements. Any thermometer may be taken, provided that in the first place its particular scale has been standardized by comparing it with that of the gas thermometer. According to the case, there will be advantage in employing one or another method; practically also one almost never employs the gas thermometer by reason of the difficulties inherent in its use, which result principally from its great dimensions and the onerous manipulation required.

For the estimation of very high temperatures the gas scale can be used only by an indirect extrapolation in terms of some property of matter whose variation has been studied within the range of the gas scale attainable experimentally and which variation is assumed to obey the same law at temperatures beyond which control cannot be had with the gas thermometer.

The fact that certain of the radiation laws, to which resort must be had for the estimation of the highest temperatures, have a thermodynamic basis and may therefore be considered an extension of the thermodynamic scale, is of the greatest importance in the extrapolation for temperatures above the attainable limit of the gas scale.

There are several series of temperature measurements on the gas scale in good agreement to 1100° C., and two series reaching nearly to 1600° C. which differ by 25° at this temperature. Beyond 1600° C. the most infusible substances permanently alter their properties, and we are forced to measure temperature in terms of the radiations coming from heated bodies for the reason that we have not been able to find any other than the radiating properties of such excessively heated bodies whose variations can be measured without destroying or permanently altering either the substance used as pyrometer or the substance examined. Perhaps also chemical methods may be employed eventually.

It is in the realm of the laws of radiation and their applications to pyrometric methods that some of the most recent and important advances in high-temperature measurements have been made, so that, with certain restrictions which will be treated in the chapter on the laws of radiation, it is possible to measure on a common scale the temperatures of bodies heated to the highest attainable limits.

It is our purpose, in this introduction, to pass in review rapidly the different pyrometric methods (that is to say, thermometers utilizable at high temperatures) whose employment may be advantageous in one or another circumstance; we shall then describe more in detail each of them, and shall discuss the conditions for their employment. But in the first place it is necessary to define within what limits the different scales may be compared to that of the normal gas thermometer; it is the insufficiency of this comparison which is still to-day the cause of the most important errors in the measurement of high temperatures.

Fixed Points. — The standardization of the different pyrometers is the most frequently made by means of the fixed points of fusion and ebullition which have been determined in the first place by means of the gas thermometer; the actual precision of the measurements of high temperatures is entirely subordinate to that with which these fixed points are known; this precision was for a long time most unsatisfactory because these fixed points could only be determined in an indirect manner with the gas thermometer, and some of them only by aid of processes of extrapolation, always very uncertain. Recent researches, however, by various observers, in which improved methods of heating have been used, as well as greater purity of materials and more carefully constructed and calibrated apparatus, have led to much more concordant results, in the determination of fixed points, even by most varied methods.

Violle was the first to make a series of experiments of considerable temperature range, which up to the last few years were our most reliable data on the question. In a first series of researches he determined the specific heat of platinum by direct comparison with the air thermometer between the temperatures of 500° and 1200°. He made use indirectly of the relation thus established between specific heat and temperature to determine by comparison with platinum the points of fusion of gold and silver; then, by extrapolation of this same relation, the points of fusion of palladium and of platinum.

	Ag[*]	Au	Pd	Pt
Fusion	*954°*	*1045°*	1500°	1779°

Finally, in a second series of experiments, he determined by direct comparison with the air thermometer the boiling point of zinc.

	Zn
Boiling point	*929.6*

Barus, when physicist of the United States Geological Survey, determined the boiling points of several metals by means of thermoelectric couples standardized against the air thermometer.

	Cd	Zn
Boiling point	*772°* and *784°*	*926°* and *931°*
Mean	*778°*	*928.5°*

Callendar and Griffiths, by means of a platinum resistance thermometer calibrated up to 500° by comparison with the air thermometer, have determined the following points of fusion and ebullition:

	Sn	Bi	Cd	Pb	Zn
Fusion	*232°*	*270°*	*321°*	*328°*	*419°*

	Aniline	Naphthaline	Benzophenone	Mercury	Sulphur
Boiling point under 760 mm.	*184.1°*	*217.8°*	*305.8°*	*356.7°*	*444.5°*

These last figures may be compared with Regnault's, and Crafts' previous determinations with the gas thermometer:

Naphthaline	Benzophenone	Mercury	Sulphur
218°	*306.1°*	*357°*	*445°*

Heycock and Neville, employing the same method, but with extrapolation of the law of resistance for platinum established at that time only up to 450°, determined the following points of fusion:

Sn	Zn	Mg (99.5%)	Sb	Al (99%)	Ag	Au	Cu
232°	*419°*	633°	629.5°	654.5°	960.5°	1062°	1080.5°

---

[*] We shall use figures in italics for all fixed points determined in terms of the gas thermometer without extrapolation.

Also using the platinum thermometer calibrated at 0, 100, and 444.7° C. (the sulphur boiling point), Waidner and Burgess more recently at the Bureau of Standards find the following:

FREEZING POINTS

Sn	Cd	Pb	Zn	Sb	Al	Ag_3–Cu_2	Ag	Cu–Cu_2O	Cu
231.9	*321.0*	*327.4*	*419.4*	630.7	658.0	779.2	960.9	1063.2	1083.0

BOILING POINTS

Naphthaline	*218.0°*	Benzophenone	*306.0°*

Jaquerod and Wassmer, using a hydrogen thermometer of 66 c.c. bulb, find:

Boiling	Naphthaline	*217.7°*	Benzophenone	*305.4°*

One of the most important standardizing temperatures is the boiling point of sulphur to which the value *444.6°* C. should be assigned from the work of some half-dozen investigators.

At the Physikalisch-Technische Reichsanstalt the question of establishing a temperature scale has received deserved attention. In the early nineties Holborn and Wien, using a thermocouple calibrated in terms of a porcelain-bulb nitrogen thermometer as far as 1400°, found the fusing points:

	Ag	Au	Pd	Pt
Fusion	*970°*	*1072°*	1580°	1780°

These results for Ag and Au were subsequently found to be high by Holborn and Day, who, after trying porcelain, worked with a platinum-iridium-bulb nitrogen thermometer and thermocouple, employing electric heating, two improvements that greatly increased the accuracy. In fact, the return to metal bulbs in place of porcelain, and the introduction of electric heating in place of gas, may be considered the inauguration of modern gas pyrometry. Holborn and Day determined the following on the constant-volume gas scale:

	Cd	Zn	Sb	Al	Ag	Au	Cu
Fusion	*321.7°*	*419°*	*630.5°*	*657.5°*	*961.5°*	*1064°*	*1084°*

This scale, commonly known as the Reichsanstalt scale, was extended to 1600° by Holborn and Valentiner, who, using extrapolation by a spectral radiation method, obtained the further fixed points:

Fusion.........Palladium = 1575°   Platinum = 1782°

The most recent determinations (1911) of boiling and freezing points are due to Holborn and Henning:

Naphthaline = 217.9_6, Benzophenone = 305.8_9, Sulphur = 444.5_1
Tin = 231.8_3, Cadmium = 320.9_2, Zinc = 419.4_0

Day, Clement, and Sosman, working at the Geophysical Laboratory of the Carnegie Institution, have further improved the constant-volume gas thermometer by eliminating the pressure of the gas on the bulb and substituting a Pt-Rh for a Pt-Ir bulb and so reducing the contamination of the comparison thermocouples caused by evaporation of iridium. Their final temperatures of fusion are for the metals they studied:

Cd	Zn	Sb	Al	Ag	Au	Cu	Ni	Co	Pd	Pt
320.0	418.2	629.2	658.0	960.0	1062.4	1082.6	1452	1490	1549	1755

Mr. Daniel Berthelot, in a series of most skillfully executed investigations extending over several years, has calibrated thermocouples by comparison with a special form of gas thermometer, making use of the variation of the index of refraction with density. In this way he has found the points:

	Ag	Au	
Fusion..............................	962°	1064°	
	Se	Cd	Zn
Ebullition.........................	690°	778°	918°

Besides these primary measurements there are some very important secondary determinations, which will be discussed later.

We may call attention, however, at this point to some of the estimations of very high temperatures obtained by extrapolating the Reichsanstalt scale by means of the radiation laws. The palladium and platinum melting points have been so determined by Nernst and Wartenberg:

Palladium = 1541°   Platinum = 1745°

Again, Wartenberg, using a vacuum tungsten resistance furnace, finds by the same method:

Ir	Rh	90 Pt-10 Rh	W
2360°	1940°	1830°	2900°

Finally, Waidner and Burgess, also using optical methods, find:

Pd	Pt	Ta	W
1546°	1753°	2910°	3050°

Even the boiling points of some of the refractory metals have been determined, although the melting points are to be preferred as high-temperature fixed points. We may cite the very skillfully executed boiling-point measurements of Greenwood made with an optical pyrometer:

Al	Sb	Bi	Cr	Cu	Fe	Pb	Mg	Mn	Ag	Sn
1800°	1440°	1420°	2200°	2310°	2450°	1525°	1120°	1900°	1955°	2270°

From all the results at hand we may conclude that the fixed points possessing the greatest reliability for the indirect standardization of the various thermometric scales and thus for the calibration of pyrometers are the following:

	Sn	Zn	Sb	Al	Ag	Au	Cu	Pd	Pt	Ir	W
Fusion....	*232°*	*419°*	*631°*	*658°*	*961°*	*1063°*	*1083°*	*1550°*	1755°	2300°	3000°

	Naphthaline	Benzophenone	Sulphur
Ebullition.......	*218.0°*	*306.0°*	*444.6°*

We may consider the high-temperature scale as known with an accuracy better than:

0.5°...........................	between	200°	and	500° C.
2.............................	"	500	"	800
3.............................	"	800	"	1100
15............................	"	1100	"	1600
25............................	"	1600	"	2000
50............................	"	2000	"	2400
100...........................	"	2400	"	3000

A more detailed discussion of the determination of fixed points and their reliability and ease of reproduction will be found in Chapter XI on Standardization.

Pyrometers. — There have been a great number of pyrometric methods proposed, among which we shall dwell only upon those which have had considerable use or promise to be useful.

Gas pyrometer (Pouillet, Becquerel, Sainte-Claire-Deville, Barus, Chappuis, Holborn, Callendar, Day). — Utilizes the measurement of change in pressure of a gaseous mass kept at constant volume. Its great volume and its fragility render it unsuitable for ordinary measurements; it serves only to give the definition of temperature and should only be used to standardize other pyrometers.

Calorimetric Pyrometer (Regnault, Violle, Le Chatelier, Siemens). — Utilizes the total heat of metals, platinum in the laboratory and nickel in industrial works. Is to be recommended for intermittent researches in industrial establishments because its employment demands almost no apprenticeship and because the cost of installation is not great.

Radiation Pyrometer (Rosetti, Langley, Boys, Féry). — Utilizes the total heat radiated by warm bodies. Its indications are influenced by the variable emissive power of the different substances. Convenient for the evaluation of very high temperatures which no thermometric substance can withstand (electric arc, sun, very hot furnaces), or when it is not convenient to approach the body whose temperature is wanted. Can be made self-registering.

Optical Pyrometer (Becquerel, Le Chatelier, Wanner, Holborn-Kurlbaum, Morse).— Utilizes either the photometric measurement of radiation of a given wave length of a definite portion of the visible spectrum, or the disappearance of a bright filament against an incandescent background. Its indications, as in the preceding case but to a much less degree, are influenced by variations in emissive power. The intervention of the eye aids greatly the observations, but diminishes notably their precision. This method is mainly employed in industrial works for the determination of the temperatures of bodies difficult of access — for example, of bodies in movement (the casting of a metal, the hot metal passing to the rolling mill). Can be used to estimate the highest temperatures and is the best method for use above 1700° C. in laboratory and works.

Electric Resistance Pyrometer (Siemens, Callendar, Waidner and Burgess). — Utilizes the variations of electric resistance of metals (platinum) with the temperature. This method permits of very precise measurements to 1000° C., but requires the employment of fragile apparatus. It merits the preference for very precise investigations in laboratories. As a secondary instrument for the reproduction of a uniform temperature scale throughout the range in which the platinum resistance thermometer can be used, to 1000° except in very heavy wire, it is unsurpassed in precision and sensibility. It is also now constructed in convenient form for industrial use.

Thermoelectric Pyrometer (Becquerel, Barus, Le Chatelier). — Utilizes the measure of electromotive forces developed by the difference in temperature of two similar thermoelectric junctions opposed one to the other. In employing for this measurement a Deprez-d'Arsonval galvanometer with movable coil, one has an apparatus easy to handle and of a precision amply sufficient for industrial and many scientific uses. With a potentiometer, an instrument is obtained of the most considerable precision, available for use to 1600° C., or even to 1750° with proper precautions. This pyrometer was used for a good many years in scientific laboratories, before it spread into general industrial use, where it also renders most valuable service.

Contraction Pyrometer (Wedgwood). — Utilizes the permanent contraction that clayey materials take up when submitted to temperatures more or less high. It is employed to-day only in a few pottery works.

Fusible Cones (Seger).— Utilize the unequal fusibility of earthenware blocks of varied composition. Give only discontinuous indications. Such blocks studied by Seger are spaced so as to have fusing points distant about 20°. In general use in pottery works and in some similar industries.

There are a number of other pyrometers which have been found suitable in special cases or which for one reason or another have been found convenient in some particular line of work. Some of these we shall mention, among them being the meldometer (Joly), interesting to the chemist or mineralogist for determining fusing temperatures of minute specimens; the various industrial instruments based on the relative expansion of metals or of a metal and graphite used in air blasts and metal baths; and, finally, pyrometers based on the flow or on the pressure of air or vapor (Hobson, Uhling-Steinbart, Job, Fournier).

Recording Pyrometers (Sir Roberts-Austen, Callendar, Le Chatelier, Siemens and Halske). — Finally, we shall describe in some detail the application of registering methods to pyrometry both for technical and laboratory installations, — a field that has been cultivated very intensively in recent years.

CHAPTER I.

STANDARD SCALE OF TEMPERATURES.

We have seen that temperature is not a measurable quantity: it is merely comparable with respect to a scale arbitrarily chosen. The normal or ideal standard scale is the *thermodynamic scale;* but as it is impossible to realize rigorously this scale, it is necessary to have a practical one. In the same way that, besides the theoretical definition of the meter, there is a practical standard, a certain meter kept at the Bureau International des Poids et Mesures, there exists, besides the ideal scale of temperatures, a practical scale, which is that of a certain gas thermometer which we are going to study. We shall first discuss the gas laws in so far as is necessary for our purpose, and then show how exactly these laws are obeyed by the actual gases that may be used in defining the temperature scale in the several possible ways.

Laws of Mariotte and Gay-Lussac. — The laws of Mariotte (or Boyle) and of Gay-Lussac are the basis for the use of the dilatation of gases for the determination of temperatures. These two laws may be written

$$\frac{p_1v_1}{p_0v_0} = \frac{1 + \alpha t_1}{1 + \alpha t_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

in which we may assume for the present that the temperatures are being measured with the mercury thermometer from 0° C. α is a numerical coefficient, the same for all gases, at least to a first approximation, and its value is about

$$\alpha = 0.00366 = \frac{1}{273}$$

when it is agreed that the interval between the temperatures of melting ice and boiling water is 100°.

But instead of considering the formula (1) as the expression of an experimental law joining the product pv to the temperature defined by the mercury thermometer, we may require of experiment merely the law of Mariotte and write *à priori* the formula in question, giving a new definition of temperature approximating that of the mercury thermometer. This new scale has the advantage that it adapts itself to the study of very much higher temperatures. The use of this process suggested by Pouillet was carefully studied by Regnault and has since become the most common method of defining temperatures practically.

The expression for the laws of Mariotte and Gay-Lussac can be put in the form

$$pv = nR\left(\frac{1}{\alpha} + t\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

by calling n the number of units of quantity (this unit may be either the molecular weight or the gram); R the value of the expression

$$\frac{p_0 v_0}{\frac{1}{\alpha} + t_0}$$

for unit quantity of matter taken at the temperature of melting ice and under atmospheric pressure.

Gas Thermometers. — The equivalent expressions (1) and (2), which arbitrarily by convention give the definition of temperature in terms of the elastic properties of a gas, may be utilized, from the experimental point of view, in various ways for the realization of the standard thermometer.

1. *Constant-volume Thermometer.* — In the thermometer designated by this name, the volume and the mass are kept invariable.

The expression (2) then gives between the two temperatures t and t_0 the relation

$$\frac{p}{p_0} = \frac{1}{\alpha} + t_0,$$

from which

$$t - t_0 = p - p_0\left(\frac{1}{\alpha} + t_0\right). \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

2. *Constant-pressure Thermometer.* — In this case the pressure and the volume of the heated mass remain constant, but the mass is variable; a part of the gas leaves the reservoir. The expression (2) then gives

$$1 = \frac{n}{n_0} \cdot \frac{\frac{1}{\alpha} + t}{\frac{1}{\alpha} + t_0},$$

from which

$$t - t_0 = \frac{n_0 - n}{n}\left(\frac{1}{\alpha} + t\right). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It would be much more logical, instead of the classic expressions constant-volume thermometer or constant-pressure thermometer, to say *thermometer of variable pressure*, *thermometer of variable mass*, which describe much more exactly the manner of their action.

3. *Thermometer of Variable Pressure and Mass.* — The action of this apparatus combines those of the two preceding types. A part of the gas leaves the reservoir, and the pressure is not kept constant. The expression (2) gives

$$\frac{p}{p_0} = \frac{n}{n_0} \cdot \frac{\frac{1}{\alpha} + t}{\frac{1}{\alpha} + t_0},$$

from which

$$t - t_0 = \frac{pn_0 - p_0n}{p_0n} \cdot \left(\frac{1}{\alpha} + t_0\right). \quad . \quad . \quad . \quad . \quad (5)$$

4. *Volumetric Thermometer.* — There exists a fourth method of the use of the gas thermometer which was suggested by Ed. Becquerel, and presents, as we shall see later, a particular interest for the evaluation of high temperatures. We keep the name for it given by its inventor. The determination of the temperature is obtained by two measurements made at the same temperature, and not as in the preceding methods by two measurements made at two different temperatures one of which is supposed known.

The mass contained in the reservoir is varied, and the ensuing change of pressure is observed. The expression (2) gives

$$pv = nR\left(\frac{1}{\alpha} + t\right),$$

$$p'v = n'R\left(\frac{1}{\alpha} + t\right),$$

from which

$$(p - p')\,v = (n - n')\,R\left(\frac{1}{\alpha} + t\right),$$

or

$$t = -\frac{1}{\alpha} + \frac{p - p'}{n - n'} \cdot \frac{v}{R}. \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

This necessitates a preliminary determination of the constant R.

In the particular case in which $p' = 0$, which supposes that a complete vacuum is obtained, the preceding relation becomes simpler and is

$$t = -\frac{1}{\alpha} + \frac{p}{n} \cdot \frac{v}{R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

The definitions of temperature given by these different thermometers would be equivalent among themselves and with that of the mercury thermometer if the laws of Mariotte and Gay-Lussac were rigorously exact, as used to be held, and if the expansion of mercury in glass were linear. The only advantage of the gas thermometer then would be to extend to high temperatures the scale of the mercury thermometer. In this way it was employed by Pouillet, Becquerel, and Sainte-Claire-Deville.

Experiments of Regnault. — The very precise experiments of Regnault caused a modification in the then admitted ideas concerning the mercury thermometer as well as the gas thermometer, and led to the definite adoption of the gas thermometer as standard.

In the first place these experiments established that different mercury thermometers are not comparable among themselves on account of the unequal dilatation of the differing glass employed in their construction. Thus they cannot give an invariable scale for the determination of temperature. In comparing them from 0° to 100° they do not present between these extreme temperatures very great differences, 0.30° as a maximum, but at temperatures above 100° these differences may become considerable and reach 10° to 20° or more. (See also Chap. IX.)

Constant-vol. air thermometer, $p_0=760$.	Mercury thermometer in			
	Crystal.	White glass.	Green glass.	Bohemian glass.
100°	+ 0.00°	+0.00°	+0.00°	+0.00°
150	+ 0.40	−0.20	+0.30	+0.15
200	+ 1.25	−0.30	+0.80	+0.50
250	+ 3.00	+0.05	+1.85	+1.44
300	+ 5.72	+1.08	+3.50	
350	+10.50	+4.00		

The numbers figuring in this table indicate the quantities by which it is necessary to increase or diminish the temperatures given by the air thermometer in order to have them correspond with those which were observed with the different mercury thermometers.

It was thus impossible to define the practical scale of temperatures in terms of the mercury thermometer. The use of the gas thermometer became necessary. But Regnault recognized that it was not possible to take a *single coefficient of dilatation* α independent of the *nature* of the gas, of its *pressure*, and of the *mode of dilatation* utilized. The coefficient of expansion at constant volume (β) and the coefficient of expansion at constant pressure (α) are not identical. This follows from the fact that the law of Mariotte is not vigorously exact; we have in reality

$$pv = p_0v_0 + \epsilon,$$

ϵ being a very small quantity, but not zero.

The experiments of Regnault permitted him not only to detect but to measure this variation of the coefficient of expansion. Here are, for example, the results which he found for air between 0° and 100°.

Volume constant.			Pressure constant.		
Pressure	β	$\frac{1}{\beta}$	Pressure	α	$\frac{1}{\alpha}$
266	0.003656	273.6	760	0.003671	272.4
760	3655	272.8	2525	3694	270.7
1692	3689	271	2620	3696	270.4
3655	3709	269.5			

For air at 4.5° Rankine obtained, from the experiments of Regnault, the formula

$$pv = p_0v_0 + 0.008163\frac{p - p_0}{\omega} \cdot pv$$

ω being the atmospheric pressure.

These coefficients vary also from one gas to another, as is shown by the following table, taken also from Regnault's experiments:

MEAN COEFFICIENT BETWEEN 0° AND 100°.

Volume constant.				Pressure constant.		
Pressure. mm.	β	$\frac{1}{\alpha}$		Pressure mm.	α	$\frac{1}{\beta}$
			Air.			
760	0.003665	272.8		760	0.003671	272.4
3655	3709	269.5		2620	3696	270.4
			Hydrogen.			
760	3667	272.7		760	36613	273.1
				2545	36616	273.2
			Carbon Monoxide.			
760	3667	272.7		760	3669	272.5
			Nitrogen.			
760	3668	272.6				
			Carbonic acid.			
760	3688	271.2		760	3710	296.5
3589	3860	259		2520	3845	259.5
			Sulphurous acid.			
760	3845	259.5		760	3902	253.0
				980	3980	251.3

These experiments show that the easily liquefiable gases have coefficients quite different from those of the permanent gases.

For the permanent gases the coefficients for constant volume differ much less among themselves than those for constant pressure; for the former the extreme deviation does not exceed $\frac{1}{1000}$; for the latter it is three times as great. Setting aside air, which is a mixture and which contains more easily liquefiable oxygen, the coefficients for constant volume of H_2, N_2, and CO are identical.

Finally, for hydrogen the coefficient of expansion does not vary appreciably with the pressure.

The inequality of the coefficients of expansion, however, does not prevent us from taking any gas whatever to define the scale of temperature, provided we apply to it the proper coefficient determined by experiment between 0° and 100°. The scales are identical, if the coefficients of expansion do not vary with the temperature. This is the conclusion to which Regnault came from a comparison of thermometers at constant volume, differing by their initial pressure or the nature of the gas. Here are the results obtained, starting from the fixed points 0° and 100°, by the aid of the following formulæ:

$$\begin{aligned} pv &= nRT, \\ p_0v &= nRT_0, \\ p_{100}v &= nRT_{100}, \\ \frac{p-p_0}{p_{100}-p_0} &= \frac{T-T_0}{T_{100}-T_0} = \frac{t}{100}. \end{aligned}$$

AIR THERMOMETER.

$p^\circ=751$ mm.	$p^\circ=1486$ mm.
Degrees.	Degrees.
156.18	156.19
259.50	259.41
324.33	324.20

PRESSURE = 760 MILLIMETERS.

Air thermometer.	Hydrogen thermometer.	Air thermometer.	CO_2 thermometer.
Degrees.	Degrees.	Degrees.	Degrees.
141.75	141.91	159.78	160.00
228.87	228.88	267.35	267.45
325.40	325.21	322.8	322.9

The deviations do not exceed 0.2°, a value that Regnault estimated not to exceed the limits of error of his experiments; he concluded from this that one gas may be used as well as another, and he took air for the normal thermometer.

Nevertheless his experiments on sulphurous acid had shown a very marked variation of the coefficient of expansion of this gas with the temperature. The following table gives the mean coefficient at constant volume between 0° and t° for this case:

	β
98.0	0.0038251
102.45	38225
185.42	37999
257.17	37923
299.90	37913
310.31	37893

By analogy it is permissible to suppose that a similar effect should take place with the other gases; but the differences were then too small, and the degree of precision of the methods of Regnault insufficient to detect it.

Results Obtained by Chappuis. — This effect has been demonstrated by experiments of very great precision made at the Bureau International des Poids et Mesures, at Sèvres. Chappuis has found, between 0° and 100°, systematic deviations between thermometers of hydrogen, nitrogen, and carbonic acid, filled at 0° under a pressure of 1000 mm. of mercury.

Hydrogen ther.	N ther.-H ther.	N ther.-CO_2 ther.
− 15°	−0.016°	−0.094°
0	0	0
+ 25	+0.011	+0.050
+ 50	+0.009	+0.059
+ 75	+0.011	+0.038
+100	0	0

In this table, taking as definition of the temperature the hydrogen thermometer at constant volume, the numbers in the last two columns indicate the deviations observed with the thermometers of nitrogen and carbonic acid; it is certain that these deviations are systematic. These results allow of the determination of the mean coefficients of expansion:

t	β (hydrogen)	β (nitrogen)	β (carbonic acid)
0°	....	0.00367698	0.00373538
100	0.00366254	367466	372477

Thus the coefficients decrease with rise of temperature, while remaining higher than that of hydrogen, to which they tend to approach. The more recent work of Chappuis and Harker and others in the establishment of a normal scale of temperatures for high temperatures will be discussed in the following sections.

In the interval 0° to 100°, the values given above, calculated from Chappuis' data of 1888, may not be absolutely exact, but they are probably very nearly correct. Some of the later results are given below; those marked Callendar are calculated by him from the data of Kelvin and Joule, using a modified formula; Chappuis' results are from his latest determinations (1902), while those of Lehrfeldt and Rose-Innes are calculations involving special thermodynamical assumptions.

DIFFERENCE BETWEEN SCALES OF NITROGEN AND HYDROGEN THERMOMETERS.

$t_n - t_h$, vol. = const., P_0 = 100 cms.

Temp. Cent.	Callendar. 1903.	Chappuis. 1902.	Rose-Innes. 1901.	Lehrfeldt. 1898.
+20	+.006	+.005	+.002	+.011
+40	+.009	+.008	+.002	+.017
+50	+.009	+.010	+.002	+.019
+60	+.008	+.009	+.002	+.019
+80	+.005	+.004	+.001	+.015

Normal Scale of Temperatures. — It results from these experiments that the different scales furnished by the various gas thermometers are not rigorously identical; the deviations between 0° and 100° are very small, but their existence is certain. It becomes necessary, therefore, in order to have a *scale of temperature rigorously defined*, to make a choice of the *nature* of the gas, of its *manner of dilatation*, and of its initial *pressure*.

The *normal thermometer* selected by the Bureau International des Poids et Mesures to define the practical scale of temperatures, and everywhere adopted to-day, is the *hydrogen thermometer*, operated at constant volume and filled with gas at 1000 millimeters of mercury at the temperature of melting ice.

For high temperatures this definition is inadmissible, because we would reach such pressures that the apparatus could not withstand. The use of the method at constant volume, that is to say, at invariable mass, is besides bad on account of the permeability of the coverings at high temperatures. It would be of great advantage to be able to employ a gas other than hydrogen and operate the thermometer at variable mass. Practically, it has been the custom, in most of the recent work at high temperatures, to use nitrogen gas at reduced pressure, 150 to 300 mm. of Hg at 0° C., although there has been, as yet, no formal agreement as to the gas or type of thermometer to use in defining the high temperature scale.

In the actual state of experimentation at high temperatures, it has been impossible as yet to obtain results exact to better than 1°, and indeed, practically, we are far from arriving at this accuracy for the highest temperatures measureable. It is very likely that we can, under these conditions, employ indifferently for the construction of the normal thermometer any permanent gas whatsoever that does not diffuse into or through the containing bulb. According to the preceding experiments, all the gases would have a dilatation slightly greater than that for hydrogen, and their coefficient of expansion, which decreases with rise of temperature, would approach that for hydrogen. For determining experimentally the error possible with a normal thermometer thus modified, we possess the following experimental data.

Crafts compared in the neighborhood of 1500° the expansion at constant pressure of nitrogen and carbonic acid, and found for this latter the mean coefficient 0.00368 in assuming 0.00367 for nitrogen.

The experiments were made by displacing in a Meyer's tube nitrogen by carbonic acid, or carbonic acid by nitrogen.

10 cc. N_2 displace	10 cc. CO_2 displace
10.03 of CO_2	9.95 of N_2
10.01	9.91
10.00	9.98
10.03	9.93
9.95	
10.09	Mean 9.94
Mean 10.02	

The two measurements give positive and negative differences of the same order of magnitude; but it should be noticed that the observed deviation ($\frac{4}{1000}$ on an average) hardly exceeds the possible error of observation. However it may be, carbonic acid, which differs much from the permanent gases at ordinary temperatures, no longer so differs in an appreciable degree at 1500°.

Violle made some comparative measurements on the air pyrometer used at constant pressure and constant volume in his determinations of the specific heat of platinum.

Volume constant.	Press. constant.	Difference.
1171°	1165°	6°
1169	1166	3
1195	1192	3

There was on an average a deviation of only 4° between the two modes of observation, and the greater part of this deviation should be laid to accidental variations of the gaseous mass resulting from the permeability of the coverings.

Chappuis has made an exhaustive experimental study of the divergences of gases from the normal scale at comparatively low temperatures and he finds that the coefficient of nitrogen (at constant volume) gradually diminishes as above stated (p. 21), but that at about 75° C. it reaches a limiting value equal to

$$\beta_{\text{lim}} = 0.00367330,$$

and it may be assumed that above this temperature the gas is in a perfect state.

The mean coefficient at constant volume for this gas between 0° and 100° is

$$\beta_{0-100} = 0.00367466$$

and the limiting value for an initial pressure $P_0 = 0$ is

$$\beta_{P_0=0} = 0.0036617.$$

This follows from the divergence that Chappuis and Harker found for the constant-volume nitrogen-thermometer from the normal scale of temperatures, in terms of the initial pressure; their experiments gave

$$\frac{\delta\beta}{\delta p} = 1.28.10^{-8} \text{ per mm. change in pressure.}$$

It is to be remembered that when the volume or pressure coefficient is found for any pressure, that value is, by definition, the one to use in computing the normal scale of temperatures.

The experiments of Chappuis and Harker were carried out at the International Bureau of Weights and Measures and included also a comparison of the platinum-resistance and nitrogen thermometers up to 500° C. and a determination of the sulphur boiling point, to which questions we shall return.

Such a normal scale of temperature for the nitrogen thermometer is given by finding the coefficient β, at 0° C. for a pressure P_0' which the gas would have, supposing it to remain perfect in the range 0° to 100°. If $P_0 = 100$ cm., $P_{100} = 136.7466$ cm.; whence $P_0' = 100.0086$ and $\beta = \dfrac{P_{100} - P_0'}{100\,P_0'} = 0.00367348$, if $\beta_{\text{lim}} = 0.00367330$ as stated above.

Nitrogen at constant pressure gives, according to Chappuis,

$$\frac{\delta\alpha}{\delta p} = 1.19.10^{-8} \text{ per mm.}$$

and $\alpha_{p=0} = 0.0036612.$

The divergences from the normal scale for this gas are about double those at constant volume, and the divergences between the uncorrected scale and the theoretical scale of the constant-volume thermometer, whose constants are given above and which represents the normal scale of temperatures, are proportional to the temperature measured from 100° and have the following values:

At 100°	0.000°
200	.023
300	.047
400	.070

These deviations are evidently very slight and are entirely negligible within this range for practically all pyrometric uses. We shall see, however, that at 1000° this correction may assume a certain importance.

For hydrogen, the limiting values given by D. Berthelot are:

$$\beta_{p=0} = 0.0036625,$$
$$\alpha_{p=0} = 0.0036624,$$

and the deviations of this gas from the normal scale are immaterial.

The latest results of Chappuis on the elastic properties of the various thermometric gases are given in the following table:

EXPANSION COEFFICIENTS OF THERMOMETRIC GASES ACCORDING TO CHAPPUIS.

$10^6\times$	Hydrogen.	Nitrogen.	Air.	CO_2.
β_{0-20}		3675.9		3733.5
β_{0-40}		3675.4		3729.9
β_{0-100}	3662.5_6	3674.6	3674.4_1	3726.2
$\beta_{p=0}$	3662.5_6	3661.7		3670
$\delta\beta/\delta P_0$	0	0.0128		
α_{0-20}		3677.0		3760.2
α_{0-40}		3674.9_7		3753.6
α_{0-100}	3660.0_4	3673.1_5	3672.8_2	3741.0
$\alpha_{p=0}$	3662.4_9	3661.2		3671
$\delta\alpha/\delta P_0$	0.0186	0.0119		

Where $\alpha = \frac{1}{V}\cdot\frac{dV}{dT}$ and $\beta = \frac{1}{P_0}\cdot\frac{dP}{dT}$ and $P_0 = 1000$ mm. Hg.

Jaquerod and Perrot have compared the coefficients of expansion β of several gases in a silica bulb between 0° C. and the melting point of gold and at initial pressures from 170 to 230 mm. of Hg, with the following results:

EXPANSION COEFFICIENTS AT HIGH TEMPERATURES.

Gas.	β.	Melting point of Au.	Pressure at 0° C. mm.
Nitrogen	0.0036643	1067.2	200–230
Oxygen	0.0036652	1067.5	180–230
Air	0.0036663	1067.2	230
CO	0.0036638	1067.05	240
CO_2 $p = 240$	0.0036756	1066.5	170
CO_2 $p = 170$	0.0036713		

We can then affirm that, in employing any permanent gas with any mode of dilatation, we shall not differ certainly by more than 1° at 1000° from the temperature of the normal scale, and that, with the exception of CO_2, all the permanent gases have very nearly the same expansion coefficient.

Theoretically it would be preferable to use hydrogen under reduced pressure, which would certainly not give deviations of 1° from the normal scale; but there is always the danger of the passage of this gas through the coverings and of its combustion by oxygen or oxides.

Practically it would be better to take nitrogen, whose expansion deviates little from that of hydrogen, less than the deviation of air. Callendar has suggested the use of helium or one of the other newly discovered inert, monatomic gases, such as argon, as they diverge less than nitrogen from the hydrogen scale, cannot dissociate and do not pass through metals, at least in the case of argon.

For high temperatures the normal thermometer will be, then, one of nitrogen or other inert gas.

Thermodynamic Scale. — It is defined, in terms of Carnot's principle applied to a reversible cycle working between two sources at constant temperatures, by the relation

$$\frac{Q_1}{Q_0} = \frac{T_1}{T_0}. \qquad (1)$$

1. *Approximate Expression.*—Consider Carnot's cycle formed, as is well known, of two isotherms and two adiabatics, and let us seek the quantity of heat absorbed following the isotherm T_1.

From Joule's experiments we have approximately

$$Q_1 = A\int p\,dv.$$

The laws of Mariotte and Gay-Lussac give

$$pv = R\left(\frac{1}{\alpha} + t\right),$$

where t is the temperature of the gas thermometer; then,

$$dv = -\,R\frac{dp}{p^2}\left(\frac{1}{\alpha} + t\right);$$

and $$Q_1 = -\,AR\left(\frac{1}{\alpha} + t_1\right)\cdot\int_{p_1'}^{p_1''}\frac{dp}{p} = AR\left(\frac{1}{\alpha} + t\right)\log\frac{p_1'}{p_1''}.$$

Similarly,

$$Q_0 = AR\left(\frac{1}{\alpha} + t_0\right)\log\frac{p_0'}{p_0''}.$$

Equation (1) becomes

$$\frac{T_1}{T_0} = \frac{Q_1}{Q_0} = \frac{\frac{1}{\alpha} + t_1}{\frac{1}{\alpha} + t_0}\left(\log\frac{p_1'}{p_1''} - \log\frac{p_0'}{p_0''}\right). \quad . \quad . \quad . \quad (2)$$

But the experiments on adiabatic expansion give

$$pv^\gamma = \text{const.},$$

where γ is the ratio of the specific heats at constant pressure and volume, and combining with the laws of Mariotte and Gay-Lussac,

$$p^{\gamma-1}\cdot t^{-\gamma} = \text{const.}$$

Consequently $\frac{p_1}{p_0}$ depends only on the ratio $\frac{t_1}{t_0}$, which is the same the whole length of the two isotherms. Thus

$$\frac{p_1'}{p_0'} = \frac{p_1''}{p_0''},$$

or $$\frac{p_1'}{p_1''} = \frac{p_0'}{p_0''}.$$

Equation (2) then takes the very simple form

$$\frac{T_1}{T_0} = \frac{\frac{1}{\alpha} + t_1}{\frac{1}{\alpha} + t_0};$$

that is to say, the *ratio of the absolute thermodynamic temperatures is equal to the ratio of the absolute temperatures of the gas thermometer;* and if on the two scales it is agreed to take equal to 100 the interval comprised between the temperatures of melting ice and the vapor of boiling water, we have, at any temperature, the equality

$$T = \frac{1}{\alpha} + t.$$

But this is only a first approximation, for we have employed relations that are but roughly so: the laws of Joule, Mariotte, and Gay-Lussac.

2. *Second Approximation.* — Reconsider the problem by a more exact method. Since T differs very little from $\frac{1}{\alpha + t}$, and since the laws of Mariotte and Gay-Lussac are nearly true, we write, following a method of calculation indicated by Callendar,

$$pv = RT(1 - \phi),$$

ϕ being a very small function of p and of T (thermodynamic temperature).

We have, then, between the temperature of the gas thermometer and the thermodynamic temperature, the relation

$$\frac{\frac{1}{\alpha} + t_1}{\frac{1}{\alpha} + t_0} = \frac{T_1(1 - \phi_1)}{T_0(1 - \phi_0)},$$

which will permit of passing from one scale of temperature to the other if we know the corresponding value of ϕ.

Consider, as before, Carnot's cycle, and let us determine the heat of isothermal expansion in a more exact manner, by utilizing the experiments of Joule and Thomson on the expansion through a porous plug, and those of Regnault on the deviations from Mariotte's law.

We write for this that the changes in energy between two given isothermal states are the same, either for the reversible expansion or for the expansion of Joule and Thomson.

$$Q_1 - A\int_{p_1'}^{p_1''} p\,dv = -A\,(p_1''v_1'' - p_1'v_1') + \int_{p_0'}^{p_1''} \frac{d\epsilon_1}{dp}\,dp,$$

ϵ being the very feeble change in heat of the gas accompanying its passage through the porous plug, in the experiment of Joule and Thomson. We get from this

$$Q_1 = A\int_{p_1'}^{p_1''} v\,dp + \int \frac{d\epsilon_1}{dp}\,dp \text{ (at constant temperature)}, \quad (3)$$

for $$d\,(pv) = p\,dv + v\,dp.$$

The relation $$pv = RT\,(1 - \phi)$$

gives for the value of v

$$v = \frac{RT}{p}(1 - \phi),$$

which, substituted in equation (3), leads to

$$Q_1 = ART_1 \cdot \int_{p_1'}^{p_1''} \frac{dp}{p} - ART_1 \cdot \int \phi_1 \frac{dp}{p} + \int \frac{d\epsilon_1}{dp}\,dp. \quad . \quad (4)$$

Similarly, we have

$$Q_0 = ART_0 \cdot \int_{p_0'}^{p_0''} \frac{dp}{p} - ART_0 \cdot \int \phi_0 \frac{dp}{p} + \int \frac{d\epsilon_0}{dp}\,dp. \quad . \quad (5)$$

If we introduce these values in the expression for Carnot's cycle, after division by T_1 and T_0 we should find an identity:

$$\frac{Q_1}{T_1} - \frac{Q_0}{T_0} = AR\log_e \frac{p_1''p_0'}{p_1'p_0''} - \int_{p_1'}^{p_1''}\left(AR\frac{\phi_1}{p} - \frac{1}{T_1}\cdot\frac{d\epsilon_1}{dp}\right)dp$$
$$+\int_{p_0'}^{p_0''}\left(AR\frac{\phi_0}{p} - \frac{1}{T_0}\frac{p\epsilon_0}{dp}\right)dp = 0.$$

The law of adiabatic expansion gives

$$\frac{p_1''p_0'}{p_1'p_0''} = 1, \qquad \log_e \frac{p_1''p_0'}{p_1'p_0''} = 0.$$

In order, then, that the expression reduce to an identity it is necessary that

$$\frac{1}{T}\cdot\frac{d\epsilon}{dp} = AR\frac{\phi}{p}, \quad \text{or} \quad \phi = \frac{d\epsilon}{dp}\cdot p\cdot\frac{1}{AR}\cdot\frac{1}{T}.$$

Referring to the experiments on air of Joule and Thomson, we have

$$\phi = 0.001173\cdot\frac{p_1}{p_0}\cdot\left(\frac{T_0}{T_1}\right)^3,$$

p_0 being the atmospheric pressure, and T_0 the temperature of melting ice.

This is still an approximate result, for we have depended upon the experiments of Joule and Thomson and on the law of adiabatic expansion; however, the approximation is more close. If it seems sufficient for air, it is certainly not so for carbonic acid. Neither is the formula rigorously exact for air.

Gas Scale Corrections. — Callendar has calculated the correction to make to the air thermometer readings by extrapolation up to 1000°, and he found the following results:

Readings of centigrade thermometer.	Volume constant.		Pressure constant.	
	ϕ	Δt	ϕ	Δt
0°	0.001173	0	0.001173	0
100	0.000627	0	0.000457	0
200	393	0.04	225	0.084
300	267	0.09	127	0.20
500	147	0.23	52	0.47
1000	54	0.62	12	1.19

The deviations of the air thermometer at high temperatures are thus very slight if concordance is established at 0° and 100°, and we have seen that in the case of nitrogen the experiments of Chappuis and Harker have shown the same to be true for this gas.

Callendar, in a more recent computation based upon the work of Kelvin and Joule and the experiments of Chappuis and others, arrives at the following values for the scale corrections for the best thermometric gases:

SCALE CORRECTIONS FOR GASES, ASSUMING $\theta_0 = 273.10°$.

Temperature centigrade.	Constant pressure, 76 cm.				Constant volume, $p_1 = 100$ cm.			
	Helium.	Hydrogen.	Nitrogen.	Air.	Helium.	Hydrogen.	Nitrogen.	Air.
− 150	+0.073	+0.084	+0.945	+0.901	−0.026	+0.013	+0.195	+0.186
− 100	+ .030	+ .022	+ .328	+ .314	− .012	+ .005	+ .080	+ .076
− 50	+ .009	+ .006	+ .090	+ .086	− .004	+ .002	+ .024	+ .023
− 20	+ .003	+ .002	+ .025	+ .024	− .001	+ .000	+ .007	+ .007
+ 20	− .0016	− .0009	− .0141	− .0134	+ .0008	− .0003	− .0043	+ .0041
+ 40	− .0022	− .0013	− .0195	− .0186	+ .0011	− .0004	− .0059	+ .0056
+ 50	− .0022	− .0013	− .0195	− .0186	+ .0011	− .0004	− .0059	+ .0056
+ 60	− .0021	− .0012	− .0180	− .0172	+ .0011	− .0004	− .0054	+ .0053
+ 80	− .0013	− .0008	− .0113	− .0108	+ .0007	− .0002	− .0038	+ .0034
+ 150	+ .0054	+ .0029	+ .043	+ .041	− .0031	+ .0010	+ .0143	+ .0136
+ 200	+ .0128	+ .0068	+ .101	+ .096	− .0076	+ .0024	+ .035	+ .033
+ 300	+ .0332	+ .0165	+ .243	+ .232	− .203	+ .0059	+ .088	+ .084
+ 450	+ .071	+ .034	+ .495	+ .472	− .047	+ .013	+ .189	+ .180
+1000	+ .243	+ .104	+1.53	+1.46	− .187	+ .044	+ .646	+ .616

The above table indicates that for the gases hydrogen and helium no attention need be paid to the thermodynamic correction, for it is quite negligible for the whole temperature range for these two gases. All the gases are also seen to have a greater correction at constant pressure than at constant volume. Again it is to be noted that at small initial pressures these corrections will be proportionally reduced, and finally that it is only in the most refined work that this correction need be applied, as in the establishment of a fixed point in pyrometry as the gold fusing-point.

D. Berthelot has indicated a simple method for calculating this thermodynamic correction for any gas.

For a constant-volume thermometer:

$$T - T_0 = t\left(1 - \frac{a}{373}\,\frac{100 - t}{273 + t}\right),$$

T_0 being the absolute temperature of melting ice (273.10°), T the absolute temperature sought corresponding to the centigrade temperature t given by the gas thermometer in question at an initial pressure of one atmosphere. For other pressures p the correction to t must be multiplied by $\frac{p}{76}$.

For the constant-pressure thermometer

$$T - T_0 = t\left[1 - \frac{a}{373}\,\frac{100 - t}{273 + t}\left(1 + \frac{273}{373}\,\frac{646 + t}{273 + t}\right)\right].$$

The value of a depends upon the critical constants of the gas and is

$$a = \frac{27}{64} R^2 \cdot \frac{T_c^3}{p_c},$$

where R is the gas constant $\left(\text{here } \frac{1}{273.1}\right)$, T_c and p_c the critical pressure and temperature respectively.

TABLE OF CRITICAL CONSTANTS.

	p_c	t_c	α
Carbonic acid	72.9 atm.	+ 31.3	2.188
Oxygen	50.0	−118	0.422
Air	39.0	−140	.342
Carbon monoxide	35.9	−141	.363
Nitrogen	33.6	−146	.343
Hydrogen	13.0	−240	.016
Helium	3	−268	.009

The formulæ of Berthelot give practically identical values for the thermodynamic corrections as found by Callendar. Buckingham has discussed in detail the departures of the temperature scales, both constant volume and constant pressure, given by the several gases, from the thermodynamic scale by a method similar to that of Berthelot's, but using a somewhat simpler equation of state. The most interesting results relate to the behavior of nitrogen, which is now generally used as the thermometric gas in high temperature measurements, and in Fig. 1 are given the corrections of the nitrogen thermometer at P_0 = 1000 mm. of Hg taken from Buckingham's paper.

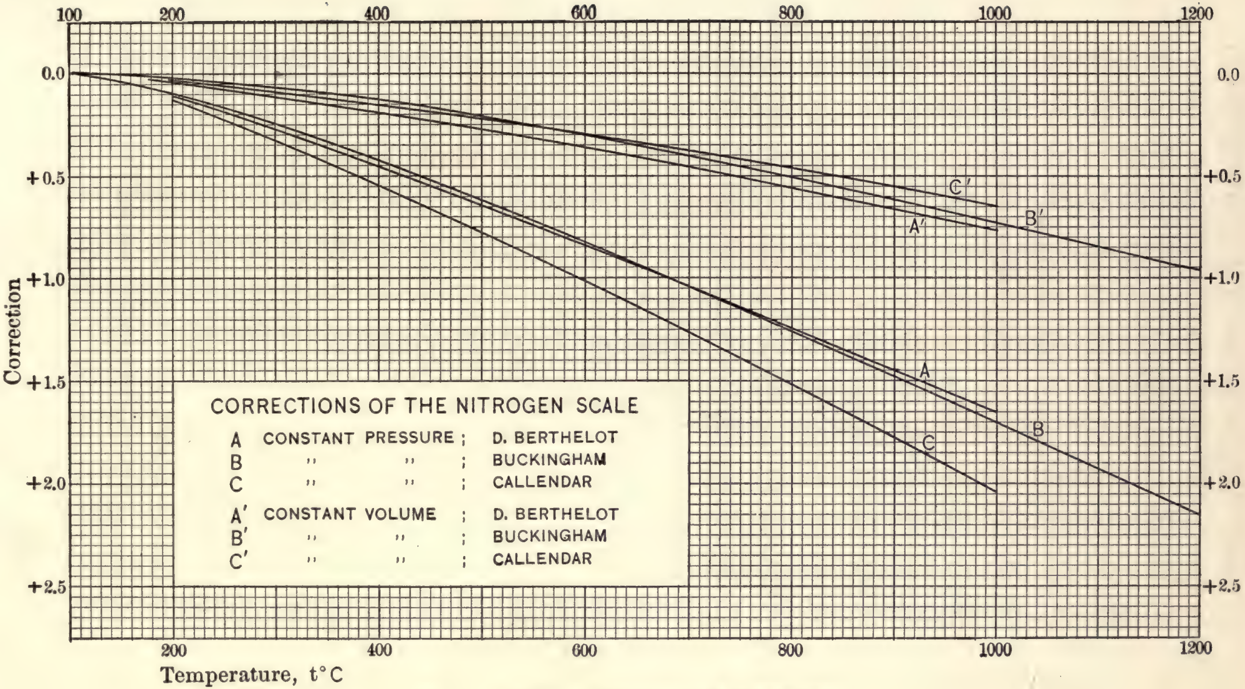


Fig. 1. · Nitrogen Thermometer Corrections.

It should be noted that the calculated corrections to reduce the readings of any gas thermometer to the thermodynamic scale are extrapolations from data on the Joule-Thomson effect made at ordinary temperatures. This is probably not a serious source of concern, however, as both Buckingham and Berthelot show that the several gases, when treated by the method of corresponding states, that is reduced in pressure and temperature to the fractions of their critical constants, furnish data all lying on the same curve.

Experimental science has now reached such a development that as above stated these corrections to the thermodynamic scale cannot always be neglected.

The Ice Point. — The experiments of Kelvin and Joule may also be used to determine the absolute temperature of the point of fusion of ice on the thermodynamic scale. Below are the results of a computation by Lehrfeldt made several years ago.

	Gas-ther.	Thermodyn. ther.
Hydrogen	273.08°	272.8°
Air	272.43	273.27
Nitrogen	273.13	273.2
Carbonic acid	268.47	274.83 (Thomson) 273.48 (Natanson)

The thermodynamic temperature of melting ice should be in all cases the same; the deviations come mainly from the uncertainties in the measurements of the heat of expansion, indicating the desirability of repeating Joule and Thomson's work with modern appliances.

There have been several more recent computations of the temperature of fusion of ice on the thermodynamic scale $\left(=\frac{1}{\alpha}\equiv\frac{1}{\beta}\right)$ based on the experimentally found deviations of several of the real gases from the ideal state, account being taken of the Joule-Thomson effect as measured by various observers, the thermal expansion and the compressibility as determined by Chappuis and by Amagat, the computations requiring the use of a modified form of Van der Waal's equation of state. Some of these calculations are as follows:

THERMODYNAMIC TEMPERATURE OF MELTING ICE (θ_0)

Author.	Gases used in computation.	θ
D. Berthelot (1903)	H, CO_2, Air	273.11
Buckingham (1907)	H, N, CO_2, Air	273.174
Rose-Innes (1908)	H	273.131
	N	273.136

The following table gives Callendar's résumé of the expansive properties of the thermometric gases. In the table θ_0 is the thermodynamic temperature of the ice-point as determined from hydrogen, and T_0 this point on the various gas scales.

EXPANSION AND PRESSURE COEFFICIENTS FOR $\theta_0 = 273.10°$.

Gas.	Constant pressure, 76 cm.			Constant volume, p_0 = 100 cm.		
	$\theta_0 - T_0$	T_0	$1/T_0$	$\theta_0 - T_0$	T_0	$1/T_0$
Helium	+0.10	273.00	.0036628	+0.19	272.91	.0036640
Hydrogen	− .135	273.235	.00365985	+ .067	273.034	.00366254
Nitrogen	+ .70	272.40	.0036708	+ .99	272.11	.00367466
Air	+ .71	272.39	.0036709	+ .96	272.14	.00367425

Chappuis' latest values give in the case of hydrogen $\frac{1}{\alpha} = 273.038$ and $\frac{1}{\beta} = 273.033$ for zero pressure on the hydrogen scale, as computed by himself, showing no sensible difference in the two hydrogen scales in the range 0° to 100° C., and, taken with the preceding tables, that the hydrogen and thermodynamic scales differ by about 0.10° C. at 0° C. Our knowledge of the thermodynamic scale, as realized by correcting the several gas scales, may be said to be in a very satisfactory condition. As we shall see in the chapter on the laws of radiation, the normal or thermodynamic scale of temperatures may be extended to temperatures indefinitely high in terms of the intensity of radiation total or monochromatic, which proceeds from a small opening in any enclosure at constant temperature throughout. We shall have realized, therefore, a single standard or normal temperature scale independent of the properties of any particular substance, continuous from the absolute zero to the highest temperatures that may be produced, and one that is practically reproducible for all technical and scientific purposes, by methods that are available in the several standardizing laboratories.

CHAPTER II.

GAS PYROMETER.

Introduction. — We have seen that the standard scale of temperatures adopted by the International Committee of Weights and Measures is given by a certain constant-volume hydrogen thermometer, namely that of the International Bureau at Sèvres, which instrument, however, has not been used to measure temperatures above 100° C. The type of gas thermometer which is to be considered standard for higher temperatures has not as yet been agreed upon by any authoritative body, but for reasons which we shall develop, the constant-volume nitrogen thermometer appears to have the preference, at least for temperatures above 200° C. From what we have seen in the preceding chapter, it is practically immaterial in the definition of the high temperature scale what form of thermometer is actually used, as the indications of any of the gas thermometers may readily be compared with those of another by well established methods of computation and reduced with great accuracy to a common theoretical basis, that of the thermodynamic scale.

It may be well to recall, at this point, in what consists the actual operation of the location of a temperature on the chosen gas scale, and point out, at the same time, some of the difficulties involved. The gas thermometer bulb must be brought throughout its volume to a sufficiently uniform temperature. To obtain a volume of 500 c.c. of gas, for example, constant in temperature to 1° at 1000° C. has not yet been attempted by any experimenter. Whatever the system of gas thermometry used, on account of the transient nature of the phenomenon measured, pressure on a manometer, a mass of displaced mercury, etc., it is also necessary, except in certain special cases as some boiling points, to bring to this same temperature some other body whose registrations are more permanent, such as a mercury, platinum resistance, or thermoelectric thermometer, or rarely a metal at its melting point, and finally it is practically necessary to transfer the readings of the gas thermometer by means of this auxiliary thermometer to a series of fixed temperatures such as freezing and boiling points. The gas scale, therefore, is found in practice to be finally a discontinuous one, or at best represented by continuous interpolations in terms of some empirical law, not the gas law. We shall see that there are further and very serious limitations in the attainment of great accuracy with the gas thermometer; thus, the space containing gas between the hot and cold parts is at an unknown average temperature; the expansion of the bulb with heat must be corrected for; and the bulb must be of sufficient rigidity and impermeability at the highest temperatures.

The gas thermometer, as we have seen above, need not of necessity be used for the measurement of temperatures; it suffices to make use of it for the standardization of the different processes employed in the determination of temperatures, but *à priori* there are not on the other hand any absolute reasons for discarding it in cases other than these standardizations. Indeed, it has often been so employed, although, as we shall see, it is usually more convenient to make use of some other method in practice.

We shall describe first the standard gas thermometer, and then discuss in considerable detail the factors that enter into the construction and theory of gas thermometers suitable for high temperatures, and give an account of several of the various investigations in gas thermometry, and finally call attention to the requirements for future work in this domain.

Standard Gas Thermometer. — This thermometer, that of the International Bureau of Weights and Measures at Sèvres, France, is a constant-volume thermometer filled with pure, dry hydrogen, under the pressure of 1 m. of mercury at the temperature of melting ice. It consists of two essential parts: the *bulb*, enclosing the invariable gaseous mass, and the *manometer*, serving to measure the pressure of this gaseous mass.

The *bulb* is made of a platinum-iridium tube whose volume is 1.03899 liters at the temperature of melting ice. Its length is 1.10 m., and its outer diameter 0.036 m. It is attached to the manometer by a capillary tube of platinum of 0.7 mm. diameter.

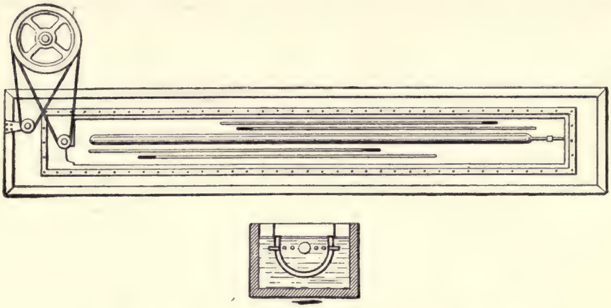


Fig. 2. Mounting of Thermometer Bulb.

A diameter of 0.5 mm. is as small as can be allowed in the colder part of such capillaries on account of the lag in obtaining pressure equilibrium.

This bulb is supported horizontally in a double box with interior water circulation. For the determination of the 100° mark, indispensable for standardization, the bulb can be placed in the same way in a horizontal heater supplied with steam and composed of several concentric coverings.

Manometer. — The manometric apparatus is mounted upon an iron support of 2.10 m. height, which is made of a railway rail firmly bolted to a tripod of wrought iron. The lateral parts attached to this rail, planed their entire length, carry sliding pieces to which are fastened the manometer tubes and a barometer. Fig. 3 represents, in a slightly modified form, the manometric apparatus. It is composed essentially of a manometer open to the air whose open arm *A* serves as cistern for a barometer *R*. The other arm *B*, closed half-way up by a piece of steel *H*, is attached to the thermometric bulb by the capillary tube of platinum *C*. The two manometer tubes, each of 25 mm. interior diameter, have their lower ends fixed into a block of steel *S*. They communicate with each other by holes of 5 mm.

diameter bored in the block. A stopcock *E* permits closing this connection. A second three-way cock *F* is screwed on the same block. One of its branches can serve to let mercury run out; the other, to which is attached a long flexible steel tube, puts the manometer in communication with a large reservoir of mercury *D* which can be raised or lowered the length of the support, either rapidly by hand, or slow-motioned by means of a screw.

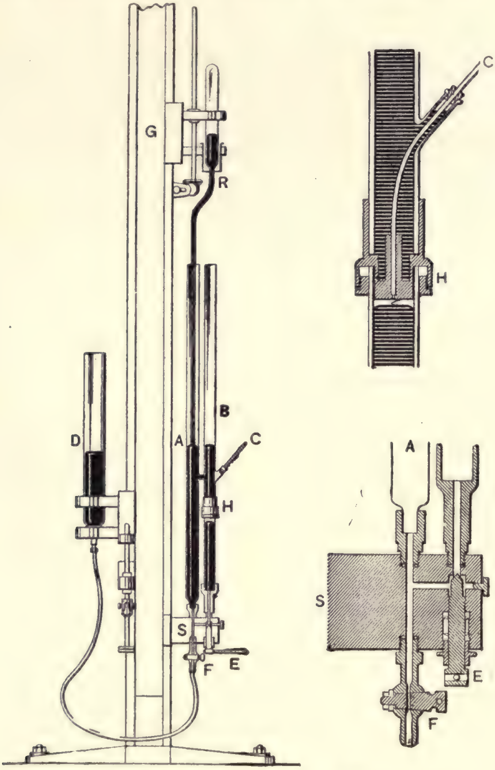


Fig. 3. Manometer of Standard Thermometer.

The barometer which sets in the open branch is fixed at its upper part on a carriage *G* whose vertical displacement is regulated throughout a length of 0.70 m. by a strong screw. The latter is held at its two ends by two nuts which permit it to turn without longitudinal motion; it works in a screw attached to the carriage, and carries at its lower end a toothed pinion which works into a cogwheel. It suffices to turn this wheel by acting upon the rod which serves as axis in order to raise or lower the carriage with the barometer tube. This last has a diameter of 25 mm. in its upper part. The chamber is furnished with two indexes of black glass soldered to the interior of the tube at 0.08 m. and 0.16 m. from the end. The points of these indexes, convex downwards, coincide sensibly with the axis of the barometric chamber. The part of the barometer which fits into the open manometer arm has a diameter greater than 0.01 m., and ends below in a narrower tube curved upwards.

The piece of steel which ends the closed arm at *H* is adjusted to this tube, leaving between itself and the tube but a very slight space, which is filled with sealing wax. It rests upon the upper rim of this tube, to which it is besides pressed by leather washers tightly screwed up. At its lower end it terminates in a perfectly smooth polished plane, which is adjusted to be horizontal. In the middle of this surface, near to the opening of the canal which prolongs the joining tube, there is fixed a very fine platinum point, whose extremity, meant to be used as a reference mark, is at a distance of about 0.6 mm. from the plane surface.

Above this piece is a tube *B* of 25 mm. interior diameter, open above and connected below to the open arm of the manometer.

Since the measurement of a column of mercury is more easily made and with greater precision when the menisci whose difference of level it is desired to find are situated along the same vertical, the barometer tube *R* is bent so as to bring into the same vertical line the axis of the closed arm of the manometer and that of the barometer. Under these conditions, the communication between the two manometer arms *A* being established through *E*, the total pressure of the gas inclosed in the reservoir of the thermometer is given by the difference of level of the mercury in these superposed tubes *B* and *R*.

The measurement of the pressures is made by means of a cathetometer furnished with three telescopes, each of which is provided with a micrometer and level. The micrometer circle is divided into 100 parts; at the distance from which the manometer is read, each division of the circle corresponds to about 0.002 mm.

The method adopted for the measurement of pressures consists in determining the position of each mercury meniscus in terms of a fixed scale, hung near the manometer tubes, at the same distance as these latter from the telescopes of the cathetometer.

One of the principal difficulties arising in the measurement of pressures is that of the lighting of the menisci. The method employed by Chappuis consists in bringing up to the surface of the mercury an opaque point until its image reflected by the mercury appears in the observing telescope at a very small distance from that of the point itself. These two images being almost in contact, it is easy to set the micrometer cross-wire midway between them, at the precise point where would be the image of the reflecting surface. In order to have a very sharp image of the point, it is well to illuminate from behind by means of a beam of light passing through a vertical slit. The point and its image then stand out black on a bright background. The use of a stylus of black glass is preferable to that of a steel point on account of unchangeableness and of the greater sharpness of the edges.

The method with stylus cannot be advantageously employed except in wide tubes, where the reflecting surface of the mercury which aids in the formation of the image does not have a sensible curvature.

Dead Space. — This consists of the space occupied by the gas: (1) in that part of the capillary tube which does not undergo the same variations of temperature as the thermometric bulb; (2) within the piece of steel forming the plug which caps the closed arm of the manometer; (3) in the manometer tube between the mercury and the horizontal plane in which ends the piece of steel. The mercury is supposed to just touch the stylus serving as reference mark.

The capacity of the capillary tube has been determined by mercury calibration; it was found equal to 0.567 c.c. The length of the capillary tube being 1 m., if we deduct from this capacity that of 3 cm. of the tube which are exposed to the same temperatures as the reservoir, that is 0.015 c.c., this leaves 0.552 c.c.

The capillary tube fits for a length of 27 mm. into the piece of steel serving as plug. The total thickness of this plug is 28.3 mm.; thus the portion of the canal included between the end of the capillary tube and the lower face of the plug is 1.3 mm. in length. As its diameter is 1.35 mm., the capacity of this canal is 0.0019 c.c.

The space included between a cross section of the manometer tube passing through the stylus and the plane surface of the plug is 0.3126 c.c.

To have the total volume occupied by the gas it is necessary to add as well to this space the volume of the depressed mercury in the manometric tube caused by the curvature of the meniscus. The radius of this tube being equal to 12.235 mm., we find for this volume 0.205 c.c.

We thus have as the total of the dead space the sum of the following volumes:

	C.c.
Capacity of capillary tube	0.5520
Volume of canal in the plug	19
Capacity of the manometer tube between the stylus and the plane	3126
Volume of depressed mercury	2050
Total dead space	1.0715

When the mercury does not just touch the stylus, we shall have to add to this value 0.4772 c.c. per millimeter separation of the stylus from the top of the meniscus.

The *expansion of the metal of the bulb* was measured by Fizeau's method; this volume was found to have at different temperatures the following values:

	Liters.
−20°	1.03846
0	1.03899
20	1.03926
40	1.04007
60	1.04061
80	1.04117
100	1.04173

The *variation of the capacity of the bulb* due to changes of pressure has also been studied; per millimeter of mercury it is 0.02337 $\overline{\text{mm.}}^3$; or

For 0 mm.	0 $\overline{\text{mm.}}^3$
" 100	2.3
" 200	4.7
" 300	7.0
" 400	9.3

The zero is verified from time to time by bringing the bulb to the temperature of melting ice; there is absolute constancy even after heating to 100°. The deviation is at the most 0.03 mm. for a pressure of 995 mm.

Chappuis made a most careful calibration of four mercury in verre dur thermometers in terms of this standard gas thermometer in an apparatus such as shown in Fig. 2, and these mercury thermometers, with copies that have been made and distributed, represent to-day the practical standards of temperature in the interval − 35° to + 100° C., with an accuracy of about 0.002° C.

After a discussion of the formulæ involved, we shall consider the question of the experimental establishment of the high temperature scale, a problem which has occupied a great many able investigators for many years, and which is by no means as yet conclusively solved, there being, as we shall see, embarassing outstanding uncertainties in determinations of temperatures, for example, of 0.5° at 500° C. and some 20° at 1600° C., due wholly to experimental difficulties.

Formulæ and Corrections. — To illustrate the principles involved we shall cite as examples some of the earlier work with porcelain bulbs. As we shall see later, all of the errors here discussed have been greatly reduced in magnitude in the latest work with quartz and metal bulbs.

1. *Thermometer at Constant Volume.* — We must now render more precise the formula of the gas thermometer given in the preceding chapter by taking account of the variations of volume of the bulb, of the surrounding air temperature which changes the density of the mercury, and finally of the volume of the dead space.

We have three series of observations to make in order to determine a given temperature:

$$P_0 V_0 = n_0 R T_0, \quad \dots\dots\dots \quad (1)$$

$$P_{100} V_{100} = n_{100} R T_{100}, \quad \dots\dots\dots \quad (2)$$

$$PV = nRT. \quad \dots\dots\dots \quad (3)$$

Putting

$$T = \frac{1}{\alpha} + t,$$

the first two series serve to determine $\frac{1}{\alpha}$.

It is preferable, except in researches of very great precision, to take $\frac{1}{\alpha}$ from previously obtained results, and not to make the observations at 100°, unless one does so to check his experimental skill.

Dividing the third equation by the first, we have the relation

$$\frac{PV}{P_0 V_0} = \frac{H \Delta_0 V}{H_0 \Delta V_0} = \frac{nRT}{n_0 R T_0} = \frac{nT}{n_0 T_0}, \quad \dots\dots \quad (4)$$

where H and H_0 are the heights of mercury, Δ and Δ_0 the densities of this metal.

For a first approximation let us neglect the differences between V and V_0, n and n_0, Δ and Δ_0. We shall have then an approximate value T' for the temperature sought:

$$T' = \frac{1}{\alpha} \cdot \frac{H}{H_0}, \quad \dots\dots\dots \quad (5)$$

for

$$T_0 = \frac{1}{\alpha}.$$

Let us find now the *correction* dT to T' to obtain the exact temperature. In order to find this, take the logarithmic differential of (4):

$$\frac{dT}{T'} = \frac{d\Delta}{\Delta_0} + \frac{dV}{V_0} - \frac{dn}{n_0}. \quad \dots\dots \quad (6)$$

Then determine the values of the different terms; let t_1 and t_2 be the absolute temperatures of the surroundings when the bulb is at the temperatures T' and T_0.

1. $$\frac{d\Delta}{\Delta_0} = \frac{\Delta - \Delta_0}{\Delta_0},$$

$$\Delta = \Delta_0 \cdot [1 - k(t_2 - t_1)],$$

$$k = 0.00018(t_2 - t_1),$$

$$\frac{d\Delta}{\Delta_0} = -\ 0.00018\,(t_2 - t_1).$$

2. $$\frac{dV}{V_0} = \frac{V - V_0}{V_0},$$

$$V = V_0[1 + k'(T' - T_0)],$$

$$k'\,(\text{porcelain}) = 0.0000135,$$

$$\frac{dV}{V_0} = 0.0000135(T' - T_0),$$

by neglecting the variations of volume of the bulb due to changes of pressure.

3. $$-\frac{dn}{n_0} = \frac{x_2 - x_1}{n_0},$$

in calling x_2 and x_1 the number of molecules contained in the dead space ϵ at the temperatures t_2 and t_1. We have, in fact, N being the total mass contained in the apparatus,

$$n = N - x_2,$$

$$n_0 = N - x_1,$$

$$n - n_0 = -\ (x_2 - x_1).$$

To determine x_1 and x_2:

$$P_0\epsilon = x_1 R t_1,$$

$$P\epsilon = x_2 R t_2,$$

$$-\frac{dn}{n_0} = \frac{\epsilon}{V_0}\left(\frac{P}{t_2} - \frac{P_0}{t_1}\right) \cdot \frac{T_0}{P_0}.$$

In noting that

$$\frac{P}{P_0} = \frac{T'}{T_0},$$

we have

$$-\frac{dn}{n_0} = \frac{\epsilon}{V_0}\left(\frac{T'}{t_2} - \frac{T_0}{t_1}\right).$$

Put

$$t = \frac{t_1 + t_2}{2},$$

$$\theta = \frac{t_2 - t_2}{2}.$$

After substitution we have

$$\frac{dn}{n_0} = -\frac{\epsilon}{V_0} \cdot \left(\frac{T' - T_0}{t} - \frac{\theta}{t} \cdot \frac{T' + T_0}{t}\right).$$

These successive transformations are for the purpose of making evident from the formula:

1. The ratio of the dead space to the total volume: $\frac{\epsilon}{V_0}$;
2. The temperature measured: $T' - T_0$;
3. The variation of the surrounding temperature θ;

which are the three essential factors on which depends the correction in question.

Formula (6) then becomes:

$$\frac{dT}{T'} = -0.00018(t_2 - t_1) + 0.0000135(T' - T_0)$$

$$-\frac{\epsilon}{V_0} \cdot \left(\frac{T' - T_0}{t} - \frac{\theta}{t} \cdot \frac{T' - T_0}{t}\right).$$

Let us take a numerical example in order to show the importance of these correction terms in the three following cases:

$$T' - T_0 = 500°,$$

$$T' - T_0 = 1000°,$$

$$T' - T_0 = 1500°.$$

In taking

$$\frac{\epsilon}{V_0} = 0.01,$$

$$t = 27^\circ + 273^\circ = 300^\circ,$$

$$2\,\theta = 10^\circ,$$

we have

$$dT_{500} = -\ 1.4^\circ + \ 5.15^\circ + 13.1^\circ = \ 16.85^\circ,$$

$$dT_{1000} = -\ 2.3^\circ + 17.0^\circ \ + 38.2^\circ = \ 52.9^\circ,$$

$$dT_{1500} = -\ 30.7^\circ + 35.7^\circ \ + 90.0^\circ = 122.5^\circ.$$

These figures show the very great importance of the dead space, whose exact volume it is very difficult to determine. This method of computation of the corrections by logarithmic differentials is only approximate, and is not sufficient for real measurements, but it renders more clear the general discussion of the causes of error.

Let us see what uncertainty in the temperature may result from the uncertainty which there may be in the volume of the dead space. In reality there is a continuous passage from the high temperature of the pyrometer to the surrounding temperature on a length which may vary from 10 to 30 centimeters, according to the thickness of the walls of the furnace. The volumes of the bulb and of the dead space which should be taken in order that the above formulas be exact should be such that the real pressure is equal to the pressure that would exist in supposing that a complete and sudden change of temperature took place at a definite fictitious point, separating the heated part from the cold part of the apparatus. The probable position of this point is estimated, and if the estimation is poorly made, two errors are committed, one on the real volume heated and the other on the dead space, errors equal and of opposite sign so far as the volume is concerned.

To calculate this *error*, as in the case of the corrections, we may employ the method of logarithmic differentials.

Applying the same formula as before, we find for the relative error $\frac{dT}{T}$:

$$\frac{dT}{T} = -\frac{dV}{V_0}\left(\frac{T' - T_0}{t} - \frac{\theta}{t} \cdot \frac{T' - T_0}{t}\right);$$

and neglecting the second term of the parenthesis, which is relatively very small,

$$\frac{dT}{T} = -\frac{dV}{V_0}\left(\frac{T' - T_0}{t}\right).$$

Letting the section of the capillary tube be equal to 1 sq. mm., the volume of the bulb 100 c.c., and assuming an uncertainty of 100 mm. in the position of the transition point, a value often not exaggerated, we find the following errors in the temperatures:

$$dT_{500} = 1.7^\circ,$$

$$dT_{1000} = 3.9^\circ,$$

$$dT_{1500} = 8.5^\circ.$$

We thus see that at 1000° the error resulting from the uncertainty in the origin of the dead space may reach several degrees for a bulb of 100 c.c.

A second cause of error results from the changes of mass following the ingoings and outgoings of gas. As before, we have

$$\frac{dT}{T} = -\frac{dn}{n_0}.$$

Consider the experiments of Crafts. There enters per hour at 1350° in a bulb of porcelain of 100 c.c., 0.002 grm. of water vapor, or 0.225 milligram molecules; the initial volume inclosed at the start is 4.5 milligram molecules:

$$\frac{dT}{T} = \frac{0.225}{4.5} = 0.05,$$

which leads to an error of

$$dT_{1350^\circ} = 70^\circ \text{ (about)}$$

for an experiment lasting one hour.

This computation demonstrates clearly the enormous errors which may result from the penetration of an outside gas during the time of one hour, a length of time much less than that of an ordinary experiment. It is true that this error decreases rapidly with rise of temperature, and it is very probably zero at 1000°, if there is no break in the glazing.

2. *Constant-pressure Thermometer.* — We still employ the same formula (4):

$$\frac{H\Delta V}{H_0\Delta_0 V_0} = \frac{nRT}{n_0R_0T_0},$$

which gives for a first approximation

$$\frac{T'}{T_0} = \frac{n_0}{n}.$$

Calling t_1 and t_2 the surrounding absolute temperatures corresponding to T_0 and T_1, u_1 and u_2 the corresponding volumes of the dead space and of the reservoir, we have, for the determination of n and n_0, the relations:

$$n_0 = N - x_1 = \frac{H_0\Delta_0 V_0}{t_2 \cdot t_1},$$

$$n = N - x_2 = n_0 - (x_2 - x_1),$$

$$x_2 = \frac{H\Delta u_2}{Rt_2},$$

$$x_1 = \frac{H_0\Delta_0 u_1}{Rt_1}.$$

As before, there is a correction to be applied to the approximate temperature T' thus obtained:

$$\frac{dT}{T'} = \frac{dH}{H_0} + \frac{d\Delta}{\Delta_0} + \frac{dV}{V_0},$$

an expression the values of whose terms are known.

Let us see now the causes of error and discuss their importance.

The error resulting from the uncertainty in the boundary of the hot and cold volumes is

$$\frac{dT}{T'} = \frac{dn_0}{n_0} - \frac{dn}{n} = \frac{dn}{n_0}\left(1 - \frac{T'}{T_0}\right) = -\frac{dn_0}{n_0}\left(\frac{T' - T_0}{T_0}\right).$$

As before, let

$$\frac{dn}{n_0} = \frac{1}{1000}.$$

Then we find

$$dT_{500} = 1.5^\circ,$$

$$dT_{1000} = 5.0^\circ,$$

$$dT_{1500} = 9.3^\circ.$$

Thus the errors due to this cause are still greater than by the method of constant volume.

In order to make exactly the correction for the dead space, the method of Regnault's compensator may be employed, as in the work of Sainte-Claire-Deville and Troost; this allows of placing the measuring apparatus at a considerable distance from the fire, which makes the experiments much easier.

Let us now examine the error resulting from the entrance of exterior gases:

$$\frac{dT}{T'} = \frac{dn}{n} = \frac{dn_0}{n_0}\cdot\frac{T}{T_0}.$$

For the experiment of Crafts, the error would be 413° instead of 70°, the bulb being filled at the start at atmospheric pressure.

It is thus evident that, from all points of view, the method of constant volume is more precise than that of constant pressure; the lack of impermeability of the coverings was the only hindrance preventing the use of the former in early practice.

3. *Volumenometric Thermometer.* — The volumenometer of Becquerel does not require the invariability of the gaseous mass throughout the duration of the experiment. The method consists in measuring the changes of pressure resulting from a given variation of the gaseous mass contained in the bulb. Becquerel employed very slight changes of mass; the changes of pressure are then equally slight, which diminishes the precision of the measurements.

There is no theoretical inconvenience in reaching an absolute vacuum, or, what is practically more simple, using the exhaustion given by a water pump, as was done by Mallard and Le Chatelier; this considerably increases the precision. If the exhaustion is complete, we have the relation

$$\frac{PV}{RT'} = n = \frac{P_0 u_0}{RT_0},$$

u_0 being the volume of the reservoir corresponding to the surrounding temperature T_0. If the two volumes are filled under atmospheric pressure, $P = P_0$, and then

$$\frac{T'}{T_0} = \frac{u}{V}.$$

There are two corrections to make: the first relative to the expansion of the envelope, the second to the difference between P and P_0 when the exhaustion is produced by a water pump:

$$\frac{dT}{T'} = \frac{dP}{P} + \frac{dV}{V}.$$

In general dP is in the neighborhood of 15 mm. of mercury, which gives

$$\frac{dP}{P} = 0.02.$$

Also,

$$\frac{dV}{V} = 0.0000135(T' - T_0),$$

$$\frac{dT}{T'} = -0.02 + 0.0000135(T' - T_0).$$

Calculating this correction for different temperatures, we have

$$dT_{500} = -10.4^\circ,$$

$$dT_{1000} = -8.5,$$

$$dT_{1500} = -0.35.$$

Let us compute now the error which comes from the uncertainty in the position of the line of separation of the warm part and the cold part of the apparatus; it is, besides, the only remaining one:

$$\frac{dT}{T'} = \frac{dV}{V}.$$

As before, assuming the higher limit to be $\frac{1}{1000}$,

$$\frac{dT}{T'} = \frac{1}{1000},$$

which leads to

$$dT_{500} = 0.77^\circ,$$

$$dT_{1000} = 1.27,$$

$$dT_{1500} = 2.77.$$

From the point of view of the reduction of these errors, this method is preferable to the others, but it appears to have the theoretical disadvantage of not being reducible to the thermodynamic scale.

This whole discussion of the sources of error in the measurement of temperatures aims merely to obtain a determination of the temperature of the pyrometer employed. But this temperature is in itself not the real object of the measurements; it is but an intermediary to arrive at a knowledge of the temperature of certain other bodies supposed to be in thermal equilibrium with the pyrometer. Now this equilibrium is extremely difficult to realize, and it is more often the case that there is no way of being sure of the exactitude with which it has been obtained Here is then a source of error very important in the measurement of temperatures, especially of high temperatures, at which radiation becomes an important consideration. Within an inclosure whose temperature is not uniform, which is true for the majority of furnaces, there may exist enormous differences of temperatures between neighboring parts. One cannot too strongly insist upon the presence of this source of error, with whose existence too many investigators have not sufficiently occupied themselves.

Substance of the Bulb. — One of the most important points to consider is the choice of the substance which constitutes the bulb; it is necessary to know its expansion to account for the variation of its volume under the action of heat; and one must be sure of its impermeability to gases under pressure.

The following substances have been used up to the present time to make these bulbs: platinum and its alloys, iridium, iron, porcelain, glass, and fused quartz.

Platinum, in spite of its high price, was employed by Pouillet and Becquerel; it has the advantage over iron in not being oxidizable, over porcelain in not being fragile. Its coefficient of expansion increases in a regular manner with temperature:

	Between 0° and 100°.	Between 0° and 1000°.
Mean linear coefficient......	0.000007	0.000009

In the course of a noted controversy between H. Sainte-Claire-Deville and E. Becquerel, the former of those savants discovered that platinum was very permeable to hydrogen, a gas whose presence is frequent in flames at points where the combustion is not complete. Unfortunately, platinum was accordingly completely abandoned. It is possible, in very many cases, to be sure of the absence of hydrogen, and the very precise experiments of Randall showed that red-hot platinum was quite impermeable to all gases other than hydrogen, even with a vacuum inside the apparatus. With electric heating there is no danger of attack of metal bulbs by furnace gases, as was feared by the early observers using other heating methods.

Alloying platinum with iridium or rhodium greatly stiffens the bulb, and Chappuis used a platinum-iridium bulb of a liter capacity in his researches on the normal gas scale; and in the later investigations of Holborn and Day at the Reichanstalt in their comparison of thermocouple indications with the nitrogen scale up to 1150° C., bulbs of this material replaced porcelain to great advantage. Alloys of 10 and 20 per cent of iridium were used, giving an extremely rigid bulb and with the walls only 0.5 mm. thick, one which undergoes no appreciable deformation after being subjected to the considerable pressures required in the constant-volume gas thermometer at high temperatures. This alloy is also impermeable to nitrogen, but must be guarded against reducing gases and silicates at high temperatures.

Holborn and Day also determined the coefficients of expansion of platinum, as well as other metals, alloys, and porcelain.

For platinum and platinum-iridium they found:

$$\text{Platinum} : \lambda \cdot 10^9 = 8868\,t + 1.324\,t^2 \text{ from } 0^\circ \text{ to } 1000^\circ;$$
$$80\text{ Pt} \cdot 20\text{ Ir} : \lambda \cdot 10^9 = 8198\,t + 1.418\,t^2 \text{ from } 0^\circ \text{ to } 1000^\circ.$$

These determinations were made on bars nearly 50 cm. long in a most carefully constructed comparator heated electrically. The uniformity of the expansion of platinum is shown by the fact that Benoït's determination by Fizeau's method in the interval 0° to 80° C. gave

$$\lambda \cdot 10^9 = 8901\,t + 1.21\,t^2.$$

So that in this case extrapolation of over 900° C. led to no serious error.

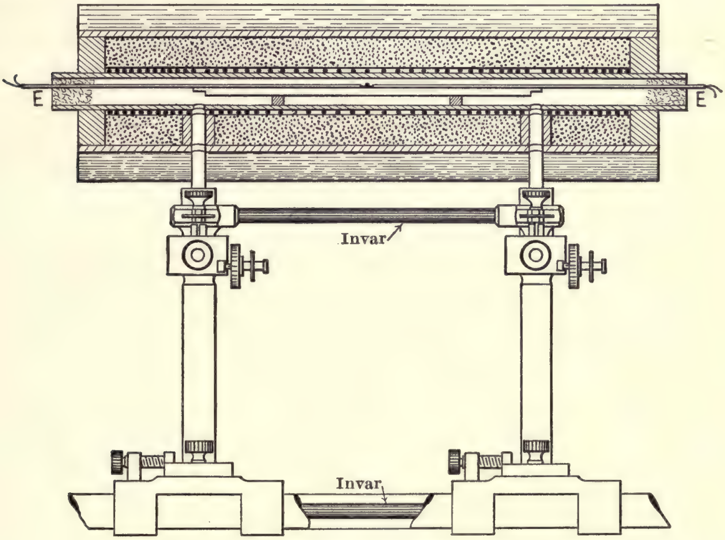


Fig. 4. Apparatus for Linear Expansion.

Day and Sosman, at the Geophysical Laboratory of the Carnegie Institution, have measured, with an improved apparatus (Fig. 4) similar to that of Holborn and Day, the expansion of the platinum alloys containing 10 per cent (10.6 by analysis) of iridium and 20 per cent of rhodium, respectively, which they have used as gas-thermometer bulbs:

90 Pt · 10 Ir : $\lambda \cdot 10^9 = 8841\, t + 1.306\, t^2$ from 300° to 1000° C.
80 Pt · 20 Rh : $\lambda \cdot 10^9 = 8790\, t + 1.610\, t^2$ from 300 to 1400

It is of interest to note that, according to these measurements, the coefficient of expansion of a platinum alloy of intermediate composition cannot be predicted by simple interpolation; therefore in any new work the actual coefficient should be determined. Holborn and Valentiner find, by a less rigorous method, however, that the expansion formula above given for 80 Pt · 20 Rh may be used to 1600° without serious error. The rhodium alloy of platinum was substituted for that of iridium at the Geophysical Laboratory for the gas-thermometer bulb material because the evaporation of iridium out of the alloy was found to be very troublesome by contaminating the thermocouple wires, in their colder parts particularly, and so changing the E.M.F. readings. The rhodium alloy is less objectionable in this respect.

Iridium. — Only one series of measurements has been made with a bulb of iridium, that of Holborn and Valentiner, and while it appeared to give results comparable with an alloy bulb, it is probably better to use the 80 Pt · 20 Rh bulb for the reason above given. Also, iridium, besides evaporating rapidly at high temperatures, is very brittle. They find for iridium to 1600° the expansion coefficient

$$\lambda \cdot 10^9 = 6697\, t + 1.158\, t^2.$$

Iron has but one apparent advantage, its cheapness; it is as permeable to hydrogen as is platinum; it is not merely oxidizable in the air, but is besides attacked by carbonic acid and water vapor. Thus the only gas that can be used with iron is pure nitrogen, and even this is questionable. The coefficient of expansion of iron is greater and increases more rapidly than that of platinum:

	Between 0° and 100°.	Between 0° and 1000°.
Mean linear coefficient....	0.000012	0.000015

Also, this increase is not regular; there is produced at 850°, at the instant of the allotropic transformation, a sudden change of length, a contraction of 0.25 per cent.

It is very difficult to obtain pure iron; very small quantities of carbon modify somewhat the value of the coefficient of expansion. Besides, the change of state of steel at 700°, corresponding to recalescence, is accompanied in the heating by a linear contraction, varying with the amount of carbon present, from 0.05 to 0.15 per cent.

Iron, therefore, cannot be considered seriously for work of any precision, and as the only excuse for working with the gas thermometer at all is to obtain the highest possible accuracy, no substance should be used for a bulb which presents any serious defects.

Porcelain was adopted as a result of the discussion between H. Sainte-Claire-Deville and Becquerel; it was considered as absolutely impermeable, but without decisive tests.

Even well-baked porcelain consists of a paste somewhat porous and permeable; it is only the glazing that assures its impermeability. But this covering may sometimes not be whole; as it softens above 1000°, it is susceptible of cracking if left for a considerable time with an excess of pressure on the interior of the apparatus. According to Holborn and Wien, the glazing is broken after reaching 1100°, when a considerable difference of pressure is established in the direction of the lifting up of this glazing.

Finally, like all verres, porcelain dissolves gases, and in particular water vapor, which passes through it quite readily. A pyrometer left a long time in the flame at about 1200° becomes filled with water vapor, which can be seen to condense in the manometer after a few weeks.

The experiments of Crafts have shown that the rapidity of the passage of water vapor through porcelain, in a pyrometer of from 60 to 70 c.c. capacity at the temperature of 1350°, was 0.002 grm. of water vapor per hour.

It is thus not safe to employ porcelain at temperatures higher than 1000°, at least not in the thermometric processes which suppose the invariability of the gaseous mass.

The expansion of porcelain has been the object of a great number of measurements which, for porcelains of very different make, give values near to one another; the mean linear coefficient between 0° and 1000° varies between 0.0000045 and 0.000005 for hard porcelain — that is to say, baked for a long time at a temperature in the neighborhood of 1400°.

Here are the results of experiments made by Le Chatelier and by Coupeaux; the experiments were made with porcelain rods 100 mm. in length, and the numbers express the elongation of these rods in millimeters:

Porcelain.	Temperatures.					
	0°	200°	400°	600°	800°	1000°
Bayeux	......	0.075	0.166	0.266	0.367	0.466
Sèvres dure (cuite à 1400°)	......	.078	.170	.270	.378	.470
Limoges	......	.076	.168	.268	.360	.465
Sèvres nouvelle (cuite à 1400°)	......	.090	.188	.290	.390	.490

These numbers should be multiplied by three to give the cubical expansion.

Porcelain has still another inconvenience; the glazing is usually put on the outside only of vessels, so that the porosity of the paste gives an uncertainty due to the unequal absorption of gases at increasing temperatures.

According to Barus, it is impossible to fill with dry air a pyrometer, not glazed inside, at ordinary temperatures. The water is not driven out by pumping out several times and letting in dry air. An apparatus filled in this way will indicate between melting ice and boiling water from 150° to 200°. Nor is filling the apparatus at 100° satisfactory: it will indicate 115° for this same interval of 100°. Barus thinks that at 400°, by repeating the operation several times, one can consider the apparatus as filled with dry air.

The use of porcelain bulbs in several recent pyrometric researches of great importance has been a cause of outstanding differences in the determination of fixed points in pyrometry as the sulphur boiling point, differences that are due mainly to the uncertainties in the expansion coefficient of the particular samples of porcelain used.

The work of Chappuis, Tutton, Bedford, and of Holborn, Day, and Grüneisen has shown the expansion of porcelain to be anomalous, and that therefore extrapolation for the coefficient cannot be made safely even over a hundred degrees for the most exact work. There is always a deformation of the bulbs of uncertain and irregular amounts in a constant-volume thermometer sufficient to render results doubtful at temperatures as low as 500° C., and Holborn and Day were unable with porcelain bulbs to get any considerable precision at 1000° C., and finally discarded them entirely.

They found for the expansion of Berlin porcelain

$$\lambda \cdot 10^9 = \{2954\,t + 1.125\,t^2\} \text{ from } 0° \text{ to } 1000°,$$

but this value is too high for temperatures below 250° as indicated by Chappuis; and Holborn and Grüneisen have shown that at about 700° C. a considerable change in the coefficient takes place, the expansion becoming more rapid at higher temperatures.

It would probably not be worth while to make further pyrometric studies with porcelain bulbs, when possible to avoid their use.

Glass cannot be used above 550° C., but to 500° C. it may replace porcelain to advantage if Jéna borosilicate 59^{III} is used, as the deformation after heating is somewhat less and more uniform. The coefficient of expansion of this glass as measured in the form of capillary tubes by Holborn and Grüneisen is

$$\lambda \cdot 10^9 = 5833\,t + 0.882\,t^2.$$

This glass was used by Holborn and Henning in 1911 to 450° with the gases nitrogen, hydrogen, and helium, to the last of which it is slightly permeable.

Jena 16^{III} glass was used by Eumorfopoulos to 445° C. Its coefficient of expansion in terms of the value of Callendar and Moss for the absolute expansion of mercury to 300° is

$$\{2385 + 1.31\,(t - 100)\}10^{-8},$$

obtained by using the thermometer bulb as a mercury-weight thermometer at 0°, 100°, and 184°. This glass has a troublesome zero lag.

Several investigations, using both constant-pressure and constant-volume thermometers, have been carried out with glass bulbs to 500° C.

Quartz glass, in the amorphous or fused form, can now be obtained in vessels of several hundred cubic centimeters capacity, thanks to many attempts culminating successfully in the effects of Heraeus, and Siebert and Kühn. The chemical and physical properties in view of its pyrometric use have been studied by many investigators, Shenstone being a pioneer in advocating its use in thermometer bulbs. Vitrified quartz vessels seem to resist deformation to fairly high temperatures, the upper limit when the interior is a vacuum being not far from 1300° C.; the substance is appreciably plastic at 1500°.

Fused quartz or silica glass is attacked by alkalies, and the slightest trace of such, as from handling, may do damage when the heating is carried very high. Weak acids and neutral salts are without effect as shown by Mylius, but at high temperatures all oxides attack it. Heated with a porcelain tube, or even alone, to temperatures above 1100° C., the quart tends to lose its transparency, cracking and changing over into a crystalline structure which readily crumbles to the touch on cooling. Water vapor even in traces hastens this process. Moissan has shown that it is slightly soluble in a lead bath above 1100° C., and very much more so in zinc. Villard showed that it is permeable to hydrogen but less so than platinum, nor does it seem to occlude other gases. It is also quite permeable to helium. Travers and Jaquerod find also that silica is reduced by hydrogen at high temperatures.

Its great advantage in gas thermometry is its lack of deformation and its extremely small coefficient of expansion, about $\frac{1}{17}$ that of platinum, or, more exactly, as determined by Holborn and Henning with a comparator,

$$\lambda \cdot 10^9 = 540\,t \text{ from } 0° \text{ to } 1000°.$$

Scheel, using a Fizeau apparatus, finds

$$\lambda \cdot 10^9 = 322\,t + 1.47\,t^2 \text{ between } 0° \text{ and } 100°,$$

where the curvature is of the same order as for metals. There is some question, however, as to the constancy of this coefficient.

In work at 1000° C. the expansion correction is reduced from over 20° with porcelain or platinum to about 1°, and its uncertainties become, therefore, negligible, permitting a great increase in accuracy. Silica glass has been used successfully by Jaquerod and Perrot as a thermometer bulb to the melting point of gold with several gases. It cannot be used continuously as an envelope, however, at temperatures much over 1100° C., for the reasons stated above.

Early Experimenters. — We shall study now the experiments made by various investigators, and we shall see in what degree the conditions of precision indicated in the course of this account have been realized.

Pouillet. — Pouillet was the first to make use of the air thermometer for the measurement of high temperatures; he obtained very good values for the epoch at which he worked.

His pyrometer was made of a platinum bulb, of ovoid form, of 60 c.c. capacity, to which was gold-soldered a platinum capillary tube of 25 cm. in length; continuous with this tube was another of silver of the same length fastened to the manometer. The joining of the platinum and silver tubes was made by means of a metal collar (Fig. 5). The dead space had thus a volume of 2 c.c.

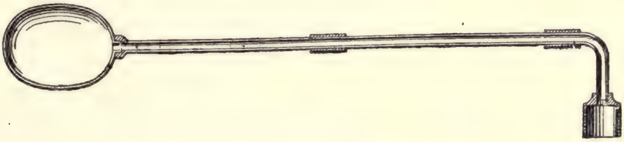


Fig. 5. Pouillet's Thermometer.

The manometer was made up of three glass tubes embedded at their lower ends in a metallic piece; the first tube serving as a measurer was graduated in cubic centimeters, the second constituted the manometer properly speaking, and the third served to fill the apparatus.

A cock conveniently placed permitted variation of the quantity of mercury contained in the apparatus (Fig. 6). The principle of this apparatus is the same as that of the more recent Regnault manometer; this latter differs from the manometer of Pouillet only in the suppression of the third tube, which is replaced by a bottle joined to the emptying cock by a rubber tube.

Pouillet's determinations of fusing points follow:

Gold	1180° (too high by 115°)
Silver	1000 (too high by 40°)
Antimony	432 (too low by 200°)
Zinc	423 (good)

Ed. Becquerel. — This savant took up and continued the work of Pouillet with the same apparatus. But at the close of a discussion with H. Sainte-Claire-Deville on the question of the permeability of platinum, he made use successively of pyrometers of iron and of porcelain. The results obtained with platinum seem, however, to be far the best.

	Pyr. of Pt.	Pyr. of Porcelain
Boiling point of zinc	930° (good)	890°
Fusing point of silver	960 (good)	916
Fusing point of gold	1092	1037

The figures for gold differ among themselves by about 25°.

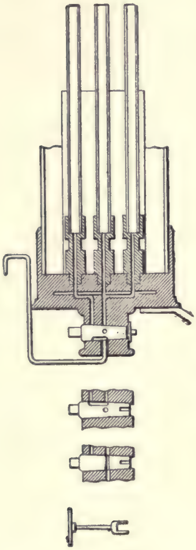


Fig. 6. Pouillet's Manometer.

Experiments of H. Sainte-Claire-Deville and Troost. — They, after their discussion with Becquerel, made numerous experiments with the porcelain air thermometer; they obtained very discordant results, which they did not publish at the time.

They placed the most confidence in the determinations made by the aid of the vapor of iodine (we shall speak of this later); but when the inaccuracy of this method was pointed out, they made known the results that they had obtained for the boiling point of zinc.

They employed a crucible of plumbago having a capacity of 15 grm. of zinc; the metal was added anew as fast as it evaporated. The crucible was placed in a furnace filled with coal. Around the pyrometer was arranged a covering of fire clay; but this arrangement was quite insufficient to eliminate errors due to radiation. The same measurements were repeated with different gases. The figures obtained for the boiling point of zinc range from *916°* to *1079°* and seem to be a function of the nature of the gas, which is inexplicable.

Violle. — Guided by H. Sainte-Claire-Deville, whom his successive failures had instructed in the difficulties of the problem, Violle made a series of measurements which were among the best for a long time. He made use of a porcelain thermometer, and he worked simultaneously at constant pressure and constant volume. The agreement of the two numbers shows if the mass has remained constant; this is the equivalent of the volumetric method of Becquerel.

The most serious objection that can be made to these observations concerns the uncertainty of the equality of temperatures of the pyrometer and of the substance studied placed beside the former; from this point of view, however, these experiments, made in the Perrot furnace, were much more satisfactory than those made in coal furnaces previously employed.

1. A first series of determinations was of the specific heat of *platinum.* A platinum mass of 423 grm. was put into a Perrot muffle alongside the pyrometer, and when the mass was in a state of temperature equilibrium it was immersed, either directly in water or in a platinum eprouvette placed, opening upward, in the midst of the calorimeter water. In the first case the experiment was made in a few seconds; in the second it lasted fifteen minutes, and the correction was as high as 0.3° per 10°; the results, however, were concordant. At 787° two experiments gave 0.0364 and 0.0366; mean, 0.0365.

At 1000° twelve experiments were made employing the method of immersion; the numbers found vary from 0.0375 to 0.0379; mean, 0.0377.

Near 1200° the measurements were made at constant pressure and at constant volume.

Temperature at Constant Volume.	Temperature at Constant Pressure.	Mean.	Specific Heat of Platinum.
1171°	1165°	1168°	0.0388
1169	1166	1168	.0388
1195	1192	1193	.0389

The mean specific heat from his observations may be represented by the formula

$$C_0^t = 0.0317 + 0.000006 \cdot t,$$

and true specific heat by

$$\frac{dq}{dt} = 0.0317 + 0.000012 \cdot t.$$

Violle used these determinations to fix, by extrapolation, the fusing point of platinum, which he found equal to 1779°. He measured for that the quantity of heat given out by 1 grm. of solid platinum from its fusing point to 0°. For this purpose a certain quantity of platinum is melted, into which is plunged a spiral wire of the same metal, and, at the instant that the surface of the bath solidifies, by aid of this wire a cake of solid platinum is lifted out and immersed in the water calorimeter.

The latent heat of fusion of platinum is equal to 74.73 c. ± 1.5; this number results from five determinations.

2. A second series of experiments was on the specific heat of *palladium;* the determinations were made, in part by comparison with platinum, in part by the air thermometer. The results obtained by the two methods are concordant.

The mean specific heat is given by the formula

$$C_0^t = 0.0582 + 0.000010 \cdot t.$$

The true specific heat is equal to

$$\frac{dq}{dt} = 0.0582 + 0.000020 \cdot t.$$

The fusing point of palladium was found equal to 1500°. The latent heat of fusion of palladium, measured by the same experiments, was found to be 36.3 calories.

3. In another series of experiments Violle determined the boiling point of zinc. He employed an apparatus of enameled casting, heated in a triple envelope of metallic vapor; the top was covered with clay and cow-hair to prevent superheating of the coverings. The measurements were made with pressure and volume simultaneously variable. He found about 930°.

4. A last series is relative to the fusing points of metals, which were determined by comparison with the total heat of platinum:

Silver	*954*°	(too low by 7°)
Gold	*1045*	(too low by 18°)
Copper (probably saturated with Cu_2O)	*1050*	(too low by 13°)

Mallard and Le Chatelier. — In their investigations on the temperatures of ignition of gaseous mixtures, Mallard and Le Chatelier made use of a porcelain pyrometer, which was exhausted; then air was let in and the gaseous volume thus absorbed was measured. It is possible to reach 1200° without noticing any breaking down of the porcelain; but this giving way is complete at 1300° under the action of the vacuum.

This method was used in the following way to measure the temperatures of ignition of gaseous mixtures: The air was exhausted from the apparatus, and the temperature was measured by the air volume which filled it; the air was again exhausted and the apparatus was filled with the gaseous mixture. Whether or not there was ignition was known by the comparison of the volume of the mixture with that of the air introduced under the same conditions of temperature, at least in the cases of mixtures burning with contraction.

The pyrometer used had a capacity of 62 c.c., after deduction of the dead space (1 c.c.); the following table gives the volumes of air corresponding to different temperatures:

400°	26.7 c.c.
600	20.6
800	16.7
1000	14.1
1200	12.2

In admitting that the measurements of volume be made to 0.1 c.c., one should have a precision of only 10° in 1000° on account of the insufficient volume of the thermometric reservoir.

Barus. — This American physicist devised a rotating apparatus, remarkable for its uniformity of temperature, but he applied it directly only to the standardization of thermoelectric couples. He worked at constant pressure. By means of couples graduated in this way, he determined the boiling points of zinc (926° to 931°) and of cadmium (773° to 784°); the boiling point of bismuth was found equal to 1200° under a reduced pressure of 150 mm., which would give under atmospheric pressure by extrapolation 1500°.

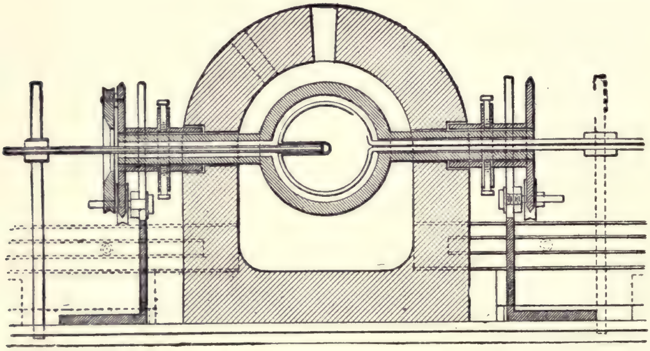


Fig. 7. Apparatus of Barus.

Fig. 7 represents the longitudinal section of Barus' apparatus. It is composed essentially of a porcelain pyrometer containing an interior tube in which is placed the couple. The pyrometer fixed at a point of its stem is held stationary. It is surrounded by a muffle of casting whose general shape is that of revolution about the axis of the pyrometer; this muffle is composed of two similar halves held by means of iron collars, and can be given a motion of rotation about its axis of figure, in such a manner as to assure uniformity of heating. It is heated by gas burners placed below. An outer covering of fire clay keeps in the heat about the iron muffle.

Holborn and Wien. — Holborn and Wien made a very complete standardization of the thermoelectric couple Pt, 90 Pt–10 Rh proposed by Le Chatelier. They made use of a porcelain reservoir of about 100 c.c. capacity, terminating at its two ends in capillary porcelain tubes. The thermoelectric junction is placed inside the bulb, and each of its wires is led out by one of the lateral tubes; this arrangement allows of determining at various points the real temperature of the dead space whose volume is 1.5 c.c.

They worked at constant volume, with a very low initial pressure so as always to have depression; they were able to reach 1430°. Above 1200° they could make but a single observation with one pyrometer; below this, about ten observations.

They determined very approximately the coefficient of expansion of their porcelain, a product of the Berlin works, and found it equal to 0.0000045, the identical number given by Le Chatelier for the Bayeux porcelain.

They made use of this pyrometer, employing as intermediary a couple, to fix the fusing points of certain metals:

Silver	*970°*
Gold	*1072*
Palladium	1580
Platinum	1780

These figures, at the time they were obtained, were counted among those which seemed to merit the most confidence; however, it is necessary to note that the volume of the bulb was too small to assure a very great accuracy, and its expansion coefficient not well known.

We shall return to these experiments when treating of electric pyrometers.

Recent Experimental Investigations. — Modern gas thermometry of precision may be said to begin with the introduction of electric furnaces, and the discarding of porcelain bulbs, both of which were effected by Holborn and Day. The constant-volume thermometer is the one almost universally used in the more recent gas thermometer researches at temperatures above 500° C., and the inclosed gas is usually nitrogen. There have been further experiments at the Reichsanstalt, where the work to 1100° C. was first repeated by Holborn and Day and then carried to 1600° C. by Holborn and Valentiner. At the Geophysical Laboratory in Washington, also, Day, Clement, and Sosman have determined a series of fixed points from zinc to palladium, using greatly improved methods for the exact determination of the higher temperatures. Jaquerod and Perrot have used several gases in quartz glass to the temperature of fusion of gold; and the hydrogen thermometer has been used by Jaquerod and Wassmer for the determination of the boiling points of naphthaline and benzophenone. The scale of the platinum-resistance thermometer has been compared with that of nitrogen to 500° C., at constant pressure by Callendar, and at constant volume by Chappuis and Harker, and by Holborn and Henning; and from these series of measurements the boiling point of sulphur has been determined by these observers and also by Eumorfopoulos, using Callendar's form of the constant-pressure thermometer.

We shall discuss in some detail most of these recent researches, in part here, and in part in the chapter on standardization.

Holborn and Day. — Their preliminary work was done with porcelain bulbs at temperatures above 500° C., using nitrogen and hydrogen and with a bulb of Jéna borosilicate glass No. 59^{III} filled with hydrogen, for temperatures below 500°. Porcelain bulbs glazed outside and also inglazed bulbs were used. Errors due to changes in the bulbs were detected by taking "zero" readings and also by the simultaneous use of thermocouples. Salt baths were used up to 700° at first, but later electric heating in air was employed in all the high-temperature work.

The hard glass bulbs of about 167 cm. capacity showed less changes, after annealing, than the irregularities in the thermocouple measurements, due to the lack of sensitiveness of the latter at low temperatures; and these glass bulbs were found preferable to those of porcelain up to 500° C. The precision attainable with thermocouple control was about 0.6° C.

Porcelain bulbs of 100 c.c. capacity, glazed inside and out, filled with hydrogen, and heated to only 700°, gave very discordant results due apparently to chemical action between the hydrogen and the walls of the bulb and to water vapor generated. Used with nitrogen and heated electrically to about 1100° C., the mean difference between the observed and calculated values was ± 1.5° C. Far less satisfactory results were obtained with porcelain glazed only on the outside.

A first series of experiments with a metal bulb were made with a 20 per cent iridium alloy of platinum, the bulbs being cylindrical, of 208 c.c. volume and 0.5 mm. wall, and the dead space was considerably reduced over that of the porcelain bulbs. The electric heating oven was also improved by winding it logarithmically so that at 1150° the temperature distribution was constant to 3° over that portion of the oven containing the bulb. This was still further equalized by the presence of the metallic bulb; also at very high temperatures the tendency to equilibrium through radiation balances more nearly the losses by end conduction. Temperature control to 0.1° C. at 1000° C. may be realized electrically with care. A precision of better than 1° C. was then obtained, and the conclusion seemed warranted that the metallic bulbs in an electrically heated furnace, where no gases or other materials acting upon platinum were in contact with it, were superior to any form of porcelain bulb.

Their later work consisted in a determination of fixed points, using the thermocouple as intermediary, after having found the coefficient of expansion of the material of their bulb and shown that the bulb underwent no deformation after heating. The correction for expansion amounts to 30° at 1000° and 40° at 1150°. The expansion was determined for a 50 cm. bar in a comparator which could be heated electrically to 1000° C.

Although no change in volume of the thin-walled bulb could be detected on cooling, a temporary yielding of the glowing walls under the comparatively high pressure might have taken place, so a bulb having walls 1 mm. thick was substituted, the composition being 90 Pt–10 Ir. This bulb was as satisfactory as the first.

The results obtained by Holborn and Day for the fixed points, as well as their work with thermoelements, will be discussed later.

Jaquerod and Perrot. — Using a quartz bulb filled at constant volume successively with nitrogen, air, oxygen, carbon monoxide, and carbonic acid, and employing an electric resistance furnace, results agreeing to 0.3° were obtained for the fusing point of gold with the first four gases, using a common coefficient of expansion based on Chappuis' limiting value and using varying initial pressures. The use of quartz reduces the correction for the expansion of the bulb to 2° at 1000°.

This work shows that in the range 0° to 1100° C. the coefficients of expansion of these gases are practically identical (see page 26).

Callendar's Constant-pressure Thermometer. — For the calibration of the platinum-resistance thermometer Callendar has studied an arrangement of the constant-pressure gas thermometer in which the dead space is reduced to a minimum by an ingenious device which consists in interposing in the capillary tube a column of sulphuric acid which is always brought to the same position (Fig. 8). It is then permissible to leave vacant spaces in the manometer of any volume, and this simplifies the measurements.

The *bulb* is of glass, and its capacity is 77.01 c.c. The capillary tube has a diameter of 0.3 mm. It is attached to a small U tube of 2 mm. diameter which contains the sulphuric acid. The total value of the waste space is thus reduced to 0.84 c.c.

The sulphuric acid before each measurement is brought up to a reference mark. The density of this liquid being one-seventh that of mercury, the errors made in determining its level should be divided by seven to express them in heights of mercury. The use of this column of sulphuric acid has the inconvenience to oblige the experimenter to watch constantly the apparatus during the whole time of heating and cooling in order to maintain the pressure equilibrium in the two parts of this column; otherwise the liquid would be driven into the manometer or absorbed into the bulb.

The *manometer* is one open to the air and is read conjointly with the height of the barometer.

The *coefficient of expansion* of the hard glass used in the construction of the thermometer was measured for a tube of same make by means of two microscopes carried upon a micrometer screw but sighted on the cold ends of the tube. A cold comparison tube could be placed under the microscopes to verify the invariability of their distance apart.

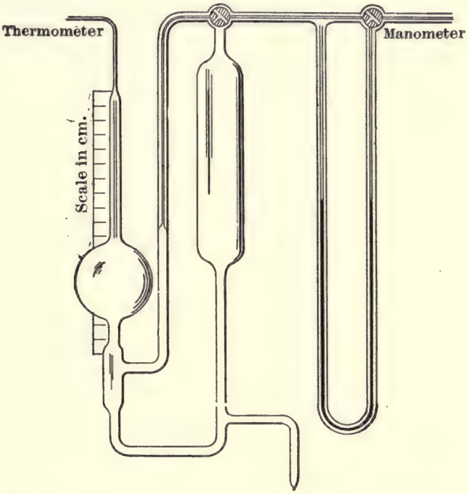


Fig. 8. Callendar's Differential Manometer.

MEAN COEFFICIENT OF EXPANSION.

t	α
17°	0.00000685
102	706
222	740
330	769
481	810

After heating to 400° there were permanent changes amounting to from 0.02 to 0.05 per 100.

If the zero is taken at intervals of time of varying length, permanent displacements are noted in the bulb. The following table gives some examples:

Date.	Oxygen Thermometer.	Nitrogen Thermometer.	Remarks.
	mm.	mm.	
Jan. 21, 1886....	693.1	695.4	Filled at 300°; measurement taken 4 days later.
Jan. 22, 1886....	692.9	695.1	
Jan. 23, 1886....	692.9	694.9	After heating to 100°.
Jan. 25, 1886....	692.0	693.8	
Jan. 25, 1886....	692.0	694.1	After heating to 100°.

This change of zero has been attributed to a partial absorption of the air by the glass. Glass, an amorphous body resembling liquids somewhat, may dissolve gases, especially at high temperatures, although this is not borne out by Holborn and Day's work on nitrogen.

For temperatures higher than 300° this source of error becomes very serious, especially if the gas is hydrogen. This gas disappears progressively by solution in the glass or by oxidation, replacing elements of the glass. It is necessary to revert to nitrogen. This fact was observed by Chappuis and Harker in the course of a study of the platinum-resistance pyrometer when the temperatures measured reached as high as 600°.

One of the more recent forms of this thermometer in which there is complete compensation of the dead space is shown in Fig. 9, where *A* is the thermometer bulb connected by a capillary *a* to an overflow bulb, or, as here shown, to a burette *B*. The compensating capillary *b* is also connected to a bulb *C*, and across the two capillaries *a* and *b* is inserted the differential manometer *D*. The bulbs *C* and *B* for most exact work should be inclosed in a bath at constant temperature, as an ice bath. The relative sizes of the bulbs for the greatest accuracy will depend upon the temperature range to be studied. When equilibrium and compensation are established at any temperature, the mass of the gas in the two parts of the apparatus will be the same if the pressures are adjusted to equality as shown by the sensitive manometer *D*, this supposing that *C* and *B* are at exactly the

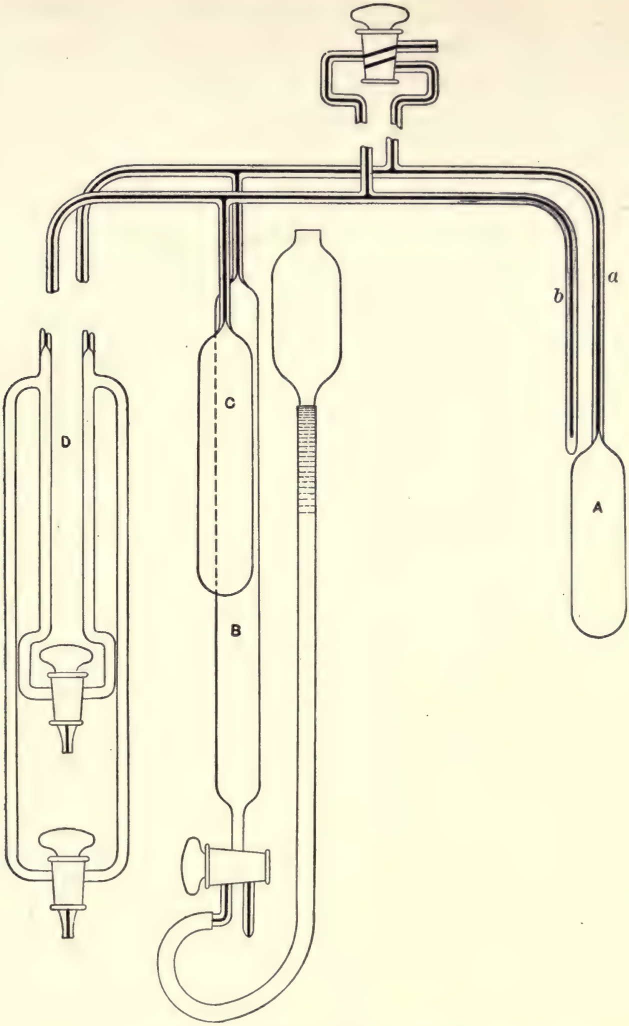


Fig. 9. Callendar's Thermometer.

same temperature. For a change in temperature the volume change of the gas in *B*, i.e., forced over from *A*, may be made by reading this volume on the burette, or better by weighing the displaced mercury. The upper stopcock serves to exhaust and fill the apparatus.

A determination of temperature, making no allowance for correction terms, is made as follows: For the compensating side of the apparatus we have

V_0 = volume of gas in C;
m_0 = mass of gas in C;
θ_0 = temperature of gas in C on gas scale;
p_0 = pressure of gas in C;
v = volume of capillaries;
θ = average temperature of capillaries.

Then

$$p_0\left(\frac{V_0}{\theta_0}+\frac{v}{\theta}\right)=mk,$$

where k is a constant.

For the thermometer proper we have, using a similar notation,

$$p_t\left(\frac{V_t}{\theta_t}+\frac{V_m}{\theta_m}+\frac{v}{\theta}\right)=m_1k,$$

the subscript $_t$ referring to A, and $_m$ to B.

But $m_1 = m$ and $p_t = p_0$ as conditions of compensation; therefore

$$\frac{V_t}{\theta_t}+\frac{V_m}{\theta_m}=\frac{V_0}{\theta_0}.$$

But C and B are at the same temperature, θ_0, or $\theta_m = \theta_0$. Finally

$$\theta_t=\frac{V_t\times\theta_0}{V_0-V_m}.$$

This type of thermometer with an air-filled porcelain bulb was used by Callendar and Griffiths to determine the boiling point of sulphur, for which temperature, after correcting for the expansion of porcelain, they obtained *444.53*° C. on the constant-pressure air scale. Eumorfopoulos, using air in a bulb of Jéna 16^{III} glass, has obtained very recently with the same type of thermometer *444.55*°, with a range in eleven experiments of 0.37° C., the thermometer bulb of 90 c.c., properly screened, being put into the sulphur vapor. A preliminary publication gave 443.58°, but this was in terms of an uncertain extrapolation of the absolute expansion of mercury from 100°, which was used to obtain the coefficient of expansion of the glass bulb to the S.B.P. The correction of +0.97° was computed by Callendar and Moss in terms of their very recent measurements of the absolute expansion of mercury to 300° C.

Eumorfopoulos gives also the exact formulæ for the use of such a thermometer. He found Jéna 16^{III} to give very troublesome changes of zero, the bulb changing in volume by about 1 per cent during the course of his experiments.

Used with a quartz-glass or platinum-alloy bulb, such a gas thermometer may become an instrument of the greatest accuracy for the experimental extension of the gas scale at constant pressure.

Holborn and Valentiner. — The need of extending the gas scale to as high temperatures as possible with modern appliances was appreciated at the Reichsanstalt, and this difficult task was first undertaken in 1906 by Holborn and Valentiner, who compared the constant-volume nitrogen scale to 1600° C. with that of the platinum-rhodium thermocouple and the optical pyrometer.

The experiments were executed with two bulbs, one of a 20 per cent iridium alloy of platinum of 208 c.c. capacity, heated in an Heræus platinum-foil resistance furnace, and one of iridium, 54 c.c. capacity, heated in an Heræus iridium-tube furnace. Initial pressures of 136 to 250 mm. were used. To avoid contamination of the wires of the single thermocouple used, they were inclosed in quartz-glass tubes. In spite of very considerable lack of uniformity of temperature within the furnace along the thermometer bulb, — as much as 60° C. in some cases, — and very considerable corrections for the dead space, — 125° to 150° at 1600° with the iridium bulb, — these observers consider their results accurate at 10° C. at the highest temperatures. We shall return to their thermoelectric and optical measurements in their respective chapters.

Day, Clement, and Sosman. — Not since the classic researches of Barus in the early eighties have serious gas-thermometer investigations been carried out in America until these experimenters (1904–10) undertook the redetermination of a series of fixed points from zinc to palladium in terms of the constant-volume nitrogen thermometer. The preliminary work of Day and Clement was done with a platinum-iridium bulb, but on account of the impossibility of completely eliminating the contaminating effects of evaporated iridium on the thermocouples, even when the latter were quartz inclosed, a bulb of 80 Pt–20 Rh was substituted in the later experiments, it having been shown by Holborn and Austin that rhodium distills from the alloy less readily in nitrogen than does iridium.

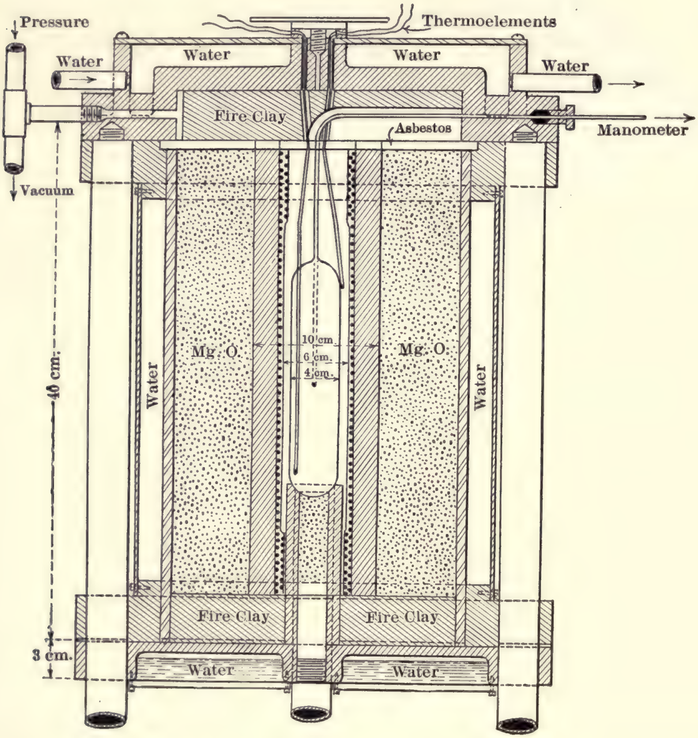
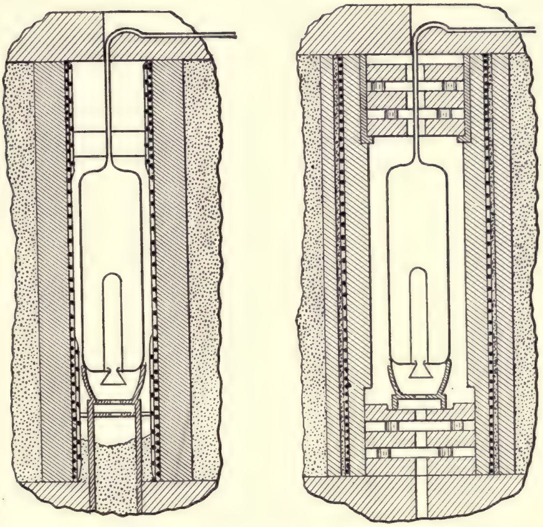


Fig. 10. Bomb Furnace and Gas Thermometer of Geophysical Laboratory.

The greatest attention was given to the perfecting of experimental methods and details of measurement, such as (1) an absolutely gas-tight bulb of constant volume, secured by having the same gas and pressure outside as within the thermometer bulb, which necessitated the conversion of the furnace into a gas-tight bomb such as shown in Fig. 10; (2) uniform distribution of temperature over the bulb during the measurements, obtained by the use of conveniently spaced and independently controlled heating coils of platinum wire and suitably adjusted diaphragms, as shown in Figs. 11 and 12, the latter being improvements over the earlier forms of furnace used at the Geophysical Laboratory; (3) the reduction to a minimum of the error due to the dead space in the capillary tube connecting the bulb and manometer, the details of which are shown in Fig. 13; (4) the exact determination of the coefficient of expansion of the bulb; and (5) the equalizing of the temperature of the manometer by air circulation. In the work of Day and Sosman, a return was made to the Barus form of reëntrant bulb (Figs. 11 and 12), and the temperature distribu-



Figs. 11, 12. Forms of Bulbs and Methods of Winding and Diaphragming.

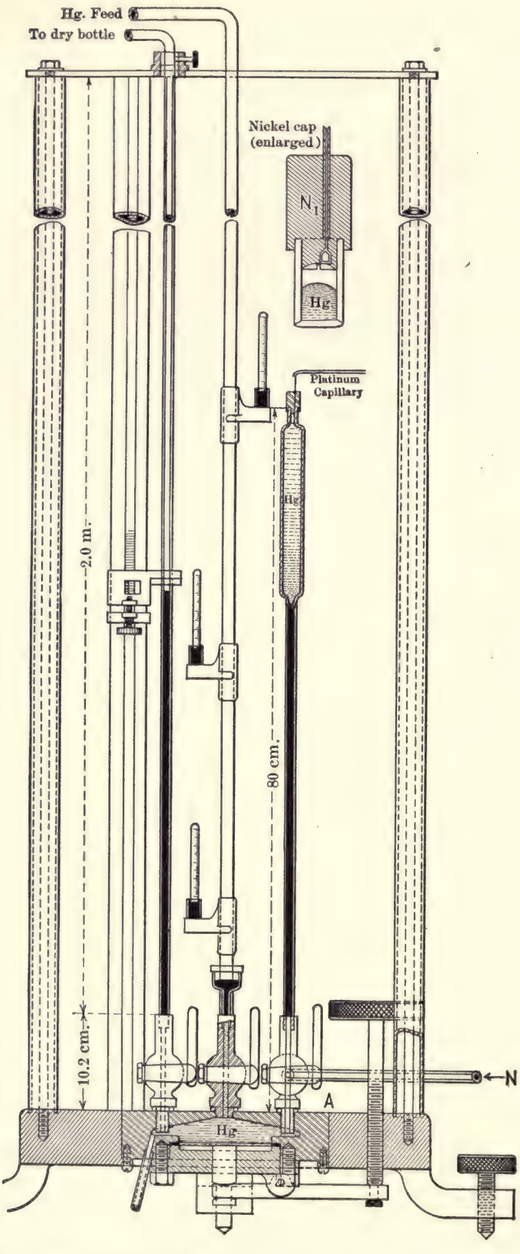


Fig. 13. Manometer of Geophysical Laboratory Thermometer.

tion over the bulb was studied by means of numerous attached platinum wires, which were used differentially, with the bulb itself as one element of a thermocouple, as well as by independent couples. The preliminary values of the silver, gold, and copper fixed points published by Day and Clement were later found by Day and Sosman to be low, mainly on account of incomplete temperature compensation along the bulb, especially at the ends.

Day and Sosman repeated the earlier work to 1100° and then determined several new fixed points, salts as well as metals, in the interval 1100° to 1600°, and consider their final results to be of great accuracy, — 0.3° at the zinc and 2° at the palladium point, — after an exhaustive study of some twenty-five possible sources of error. For measurements at 1500° C., they found, for example, the errors in the effect of the dead space $\frac{v}{V}$ reduced to 0.5°, of temperature integration over the bulb to 1.0°, and of the expansion coefficient of the bulb to 0.2°. It seems safe to say that their results are certain to 1.2° at 400° and to 10° at 1500° C.

It should be noted, however, that this gas thermometer was designed primarily for great accuracy at the highest temperatures, and as used lacks sensibility at the lower temperatures, so that the values obtained for the lower fixed points would seem to have less relative weight than for the higher ones. For example, the results of Day and Sosman, according to Waidner and Burgess, from interpolation with the resistance thermometer from the zinc point, would lead to a value of the sulphur point 1° C. lower than the value directly observed by several experimenters. The gas and resistance thermometer measurements of Holborn and Henning (1911) confirm those of Waidner and Burgess on these lower freezing points. We shall return to this question in the chapter on standardization. There is no doubt that this investigation of Day and Sosman, however, is the best that has yet been made in gas thermometry at the highest temperatures.

Comparison of Results. — It may be of interest at this point to compare some of the characteristic constants and numerical results obtained from the most recent observations, using the constant-volume nitrogen thermometer at high temperatures. The errors are those assigned by the observers.

SOME CONSTANTS AND RESULTS WITH THE NITROGEN THERMOMETER.

Observers.	Initial Pressure in mm. of Hg.	Bulb Material.	Volume of Bulb.	v/V.	Corr. for v/V at 1100° C.	Correc. for Bulb Expansion at 1100° C.	Uniformity of Temperature over Bulb.	Freezing Points.		
			c.c.					Zn	Au	Pd
Holborn and Day	286 276	80 Pt · 20 Ir 90 Pt · 10 Ir	208 196	.0042 .0046	20	43	3 to 10	419.0 ±0.5	1064.0 ±1.0	....
Jaquerod and Perrot..........	195 to 230	Quartz glass	43	.0180	70	3	2	.....	1067.2 ±1.8	....
Holborn and Valentiner......	147 137	80 Pt · 20 Ir Iridium	208 54	.0042 .022	20 90 to 110	35 30	3 to 60	....	......	1575 ±10
Day and Sosman.	217 to 347	80 Pt · 20 Rh	206	.0015	3 to 6	46	1	418.2 ±0.3	1062.4 ±0.8	1549.2 ±2.0

Suggestions for Future Experiments. — It is perhaps easier to criticize than execute experiments of precision, but from what has been said above it is evident that there is still need for more work with the gas thermometer before the high-temperature scale is established in an entirely conclusive manner. Thus, the outstanding uncertainty of nearly 0.5° at the sulphur boiling point should be eliminated; and while there is good agreement, better than 5° at 1100° C., a difference of 25° between observers exists at the palladium melting point (1550° to 1575°); and at temperatures to which it now seems hopeless to extend the gas scale directly, this range of uncertainty increases, becoming about 100° at 3000° C., or at the melting point of tungsten.

Methods. — The constant-volume method has been preferred by almost all experimenters who have worked at high temperatures, and the results by this method also have smaller corrections to reduce to the thermodynamic scale. For the lower range of temperatures at least, in view of the outstanding discrepancies, it would be well to adopt the same instrument for use both at constant pressure and constant volume. To as high temperatures as possible, the bulb should be immersed in stirred liquid baths to insure uniformity of temperature; and in this range of temperatures, or to perhaps 900°, the transfer of the gas scale can probably be made with the greatest accuracy by means of platinum-resistance thermometers, the wires of which can be made to integrate very exactly the bulb temperature.* The volumenometric method has not been used in any recent work, although it appears to possess the smallest instrumental corrections. It labors under the disadvantage of having an uncertain thermodynamic correction, but this largely disappears at high temperatures, where the outstanding uncertainties largely exceed this small correction. It would, therefore, be worth while carrying out new experiments by this method, especially at very high temperatures. The method of Crafts and Meier (p. 83) is also worthy of further study at high temperatures. The work of Day and Sosman shows that, for the constant-volume thermometer, the deformation of the bulb may be eliminated, and the error due to the dead space reduced to an almost negligible amount. Their work also shows the importance of an exact determination of the coefficient of expansion of the bulb and an exact adjustment of temperature over it by the use of properly designed electric furnaces. The uncertainty in the temperature of the manometric parts of the apparatus gives rise to an appreciable error which may be eliminated in future work by water-jacketing.

The Bulb. — All recent work has shown the superiority of the metal bulb when its coefficient of expansion is carefully determined. The alloy 80 Pt · 20 Rh is the material that has been used so far which best suits all the requirements for temperatures to 1600° C., namely, rigidity, impermeability, regular expansion, and small contaminations of the auxiliary temperature apparatus. The best form appears to be cylindrical with a reëntrant tube. It may be possible to find refractory earths which are sufficiently impermeable to use with some modification of the Crafts and

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* Both of these improvements and others have been introduced by Holborn and Henning to 450° C. since the above was written.

Meier method at very high temperatures; or possibly metallic tungsten or one of its alloys may be adopted for use in a suitable atmosphere for pushing the gas scale to the highest limits. In all cases it is desirable to have the volume of the bulb as great as possible consistent with uniform temperature distribution. To 500°, there should be no difficulty in using a 500 c.c. bulb.

The Gas. — Nitrogen has proved satisfactory in every respect, and this gas will probably be continued in use, although there would be some theoretical advantage, at least for the higher temperatures, in substituting one of the monatomic inert gases, such as argon or helium.

It is questionable whether it is worth while to attempt to extend the use of the gas thermometer above 1600° C., as the constants of the laws of radiation can be exactly determined in this range, and the radiation laws are eminently suited for extrapolation, as they give the thermodynamic scale directly.

The Manometer. — It would be well to eliminate the somewhat troublesome and uncertain reference to a variable pressure, that of the atmosphere, by the entire elimination of the barometer. This can be done, whatever the type of gas thermometer used, by evacuating to zero pressure the space above the manometer column and sealing off the manometer tube provided with a suitable globe or bulb at the top.* Variations in the temperature of the mercury columns of the manometer may be completely eliminated by water-jacketing. The errors of the manometer are then easily made negligible compared with those of expansion of the bulb, the temperature distribution over it, and the transfer to the comparison thermometer.

In general, it may be stated that it is not worth while to carry out any further gas thermometer experiments unless the utmost precautions are taken to assure the highest accuracy possible with modern appliances.

Industrial Air Pyrometers. — There have been attempts to construct air thermometers suitable for industrial usage, the argument sometimes being advanced that a gas pyrometer is

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* See note, p. 81.

per se better than any other. As we have seen, however, there is probably no physical instrument which is more difficult to employ satisfactorily, and any seeming gain in making direct use of an air thermometer for industrial use is wholly illusory. Other evident objections are fragility, uncertain correction due to the dead space, and the development of small and often unperceived leaks. Furthermore, an empirical calibration is necessary, so that such an instrument does not carry the gas scale about with itself.

Among the instruments that have been considerably used is Wiborgh's air pyrometer, shown in Fig. 14. A lens-shaped reservoir V' is open to the air before an observation is taken, but when a temperature is to be read this lens is closed to the outer air and collapsed by a lever L, thus adding a definite mass of air to the bulb V of the thermometer; the resulting pressure is transmitted to a dial as in an aneroid barometer; provision is made for automatically correcting for variations in the pressure and temperature of the atmosphere. The Bristol Company have also made industrial forms of gas pyrometer.

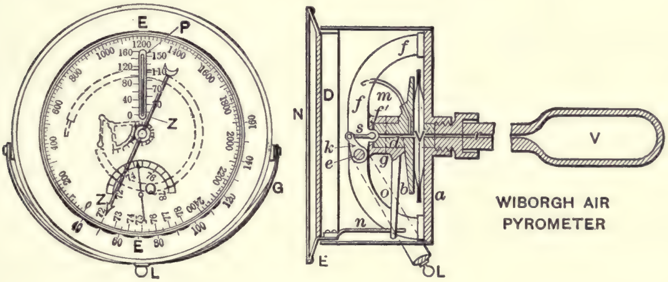


Fig. 14.

Indirect Processes. — We shall place in this list various experiments in which the laws of the expansion of gases have been used only in an indirect way, or have been extended to vapors.

Method of Crafts and Meier. — It is a variation of the method of H. Sainte-Claire-Deville and Troost, consisting in removing the gas by means of a vacuum. Crafts and Meier displaced the gas of the pyrometer by carbonic acid or hydrochloric acid, gases easily absorbable by suitable reagents. Hydrochloric acid is the more convenient, for its absorption by water is immediate; but there is to be feared at high temperatures its action on the air with formation of chlorine; it is preferable to employ nitrogen in place of air.

The apparatus (Fig. 15) consists of a porcelain bulb, whose inlet is large enough to let pass the entrance tube of the gas, which reaches to the bottom of the bulb. This arrangement increases considerably the influence of the dead space and consequently diminishes the precision of the determinations.

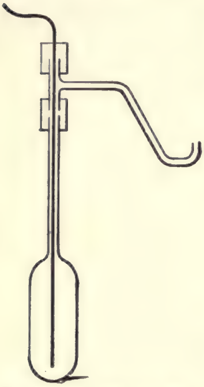


Fig. 15. Method of Crafts and Meier.

This method is especially convenient for observations on the densities of vapors which are made by the same apparatus; it then allows of having an approximate idea of the temperatures at which the experiments are made.

Crafts and Meier have in this way determined the variations in density of iodine vapor as a function of the temperature.

Regnault had previously proposed a similar method, without, however, making use of it.

1. One fills with hydrogen an iron vessel brought to the temperature that one desires to measure, and the hydrogen is driven out by a current of air; at the outlet of the metallic reservoir the hydrogen passes over a length of red-hot copper, and the water formed is absorbed in tubes of sulphuric acid in pumice stone and weighed. This method, very complicated, is bad on account of the permeability of the iron at high temperatures.

At the same time, he proposed the following method:

2. An iron bottle containing mercury is taken; the vessel, being incompletely closed, is heated to the desired temperature and then allowed to cool, and the remaining mercury is weighed.

This method is also defective on account of the permeability of iron at high temperatures; the hydrogen of the furnace gases can penetrate to the inside of the recipient and drive out an equivalent quantity of mercury vapor.

Methods of H. Sainte-Claire-Deville. — 1. This savant tried in the first place to measure temperature by a process analogous to that of Dumas' determination of vapor densities. He took a porcelain bulb full of air, and heated it in the inclosure whose temperature was wanted, and sealed it off by the oxyhydrogen flame. He measured the air remaining by opening the bulb under water and weighing the water that entered, or else he determined merely the loss in weight of the bulb before and after heating. Observations taken on the boiling point of cadmium gave 860°.

2. In a second method, which has the advantage of replacing the air by a very heavy vapor, Deville returned to the idea of Regnault, consisting in utilizing the vapor of mercury; but he ran against a practical difficulty. He had replaced the permeable iron recipients by porcelain recipients; the mercury condensed in the neck of the pyrometer and fell back in cold drops which caused the bulb to break.

For this reason he abandoned mercury and replaced it with iodine; the return of a cold liquid was completely obviated by reason of the nearness of the boiling point of this substance (175°) and its fusing point (113°). A large number of observations were made by this method; the boiling point of zinc, for example, was found to be equal to 1039°.

This method is quite faulty, as the iodine does not obey the laws of Mariotte and Gay-Lussac. The vapor density of this substance decreases with rise of temperature, this effect being attributed to a doubling of the iodine molecule. This fact was established by Crafts and Meier and confirmed by Troost.

Method of D. Berthelot. — All the preceding methods are limited by the difficulty of realizing solid envelopes resisting temperatures higher than 1600°. D. Berthelot has devised a method which, at least in theory, may be applied to any temperatures, however high, because there is no envelope for the gas, or at least no envelope at the same temperature. It is based on the variation of the index of refraction of gaseous mass heated at constant pressure; the velocity of light depends upon the chemical nature and the density of this medium, but is independent of its physical state. A gas, a liquid, or a solid of the same chemical nature produces a retardation of the light dependent only upon the quantity of matter traversed; this law, sensibly true for any bodies whatever, should be rigorously exact for substances approaching the condition of perfect gases. This retardation is measured by the displacement of interference fringes between two beams of parallel light, the one passing through the cold gas, the other through the hot gas. In reality, Berthelot employs a null method; he annuls the displacement of the fringes in changing at constant temperature the pressure of the cold gas until its density is equal to that of the gas in the warm arm which is at constant pressure.

There is a difficulty arising from the necessity of separating the light into two parallel beams, then reuniting them without imparting a difference of phase which renders the fringes invisible with white light. This is done in the following way (see Fig. 16):

A beam of light *ab* falls on a mirror MM', which breaks it up into two parallel beams, *bf* and *cd*; in order to separate the beams so as to be able to place apparatus conveniently with respect to them, a prism P gives to the beam *bf* the direction *gh*; one can thus secure a separation of 92 mm. A second prism P_1 brings the beam *cd* into *lm*, and after reflection from a second mirror, M_1M_1', the fringes are observed in a telescope focused for parallel rays. The tubes containing the gases are placed at T and T_1.

It is evidently necessary that the prisms P and P_1 be perfectly made. A preliminary adjustment is made with yellow light, then it is perfected with white light.

The tube at variable pressure is closed by two pieces of plate glass, as is also the warm tube; these four plates should be absolutely alike. The warm tube is heated by a vapor bath at low temperatures, by an electric current passing through a spiral at high temperatures.

But there is a difficulty in that in the warm tube there exists a region of variable temperature between the warm zone and the cold atmosphere.

To eliminate the influence of this variable zone, there are inside the warm tube two tubes containing running cold water, whose distance apart can be changed; it is assumed that the variable region remains the same, and that distance between the two tubes gives the warm column actually utilized. It follows that the comparative lengths of the warm column and of the cold column (this latter remaining constant) are not the same; the formula to be used will be somewhat more complicated.

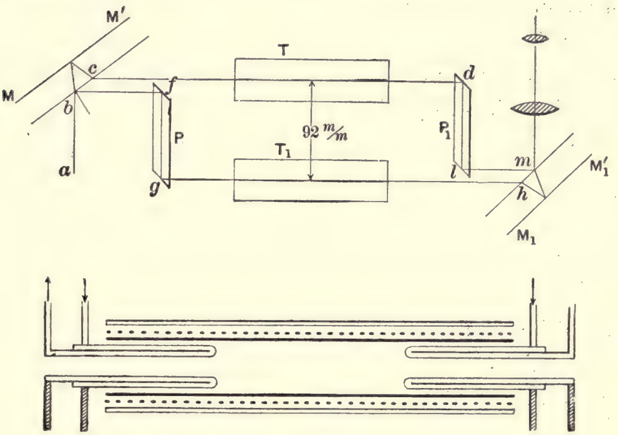


Fig. 16. D. Berthelot's Method.

n being the index of refraction of a gas and d its density, we have

$$n - 1 = kd.$$

In the constant-pressure tube

$$\frac{d_1}{d_0} = \frac{p}{p_0}.$$

To obtain the invariability of the fringes, it is necessary that

$$(n_1 - n_0)\, L = (n' - n_0)\, l,$$

L being the length of the cold tube, and l the displacement of the warm tube.

$$k\,(d_1 - d_0)\,L = k\,(d' - d_0)\,l,$$

$$L\left(\frac{d_1}{d_0} - 1\right) = l\left(\frac{d'}{d_0} - 1\right),$$

$$L\left(\frac{p}{p_0} - 1\right) = l\left(\frac{T_0}{T} - 1\right),$$

an expression which gives a relation between the pressures and the temperatures.

This method, employed for the control of the boiling points, has given the following results:

	Pressure.	Temperature observed.	Temperature calculated.
Alcohol	741.5 mm.	77.69°	77.64°
Water	740.1	99.2	99.20
Water	761.04	100.01	100.01
Aniline	746.48	183.62	183.54
Aniline	760.91	184.5	184.28

Berthelot has standardized by the same method thermocouples which he used to determine the fusing points of silver and gold, and the boiling points of zinc and cadmium:

Silver, freezing	962° C.
Gold, freezing	1064
Zinc, boiling	920
Cadmium, boiling	778

The numbers found are nearly identical with those which result from the best determinations made by other methods.

We shall discuss further the determinations of fixed points in pyrometry in Chapter XI.

CHAPTER III.

CALORIMETRIC PYROMETRY.

Principle. — A mass m of a body, brought to a temperature T, is dropped into a calorimeter containing water at a temperature t_0. Let t_1 be the final temperature of water and substance. M being the water equivalent of the substances in contact (water, calorimetric vessel, thermometer, etc.) which are raised from t_0 to t_1, L_t^T the heat required to warm unit mass of the body from t_1 to T, we have

$$L_t^T \times m = M\,(t_1 - t_0).$$

Taking as origin of temperatures the zero of the centigrade thermometer, the heat required to warm unit mass of the body to the temperature T will be

$$L_t^T = L_{t_1}^T + L_0^t.$$

The quantity L_0^t is easy to calculate, because the specific heats at low temperatures are sufficiently well known:

$$L_0^t = ct_1.$$

The expression for the total heat becomes

$$L_0^T = \frac{M\,(t_1 - t_0)}{m} + ct_1.$$

t_1 and t_0 are the temperatures given by the direct readings of the thermometer.

The value of the second member is thus wholly known, and consequently that of the first member which is equal to it. If previous experiments have made known the value of the total heat L_0^T for different temperatures, one may from the knowledge of L_0^T determine the value of T. It will be sufficient to trace a curve on a large scale whose ordinates are temperatures, and

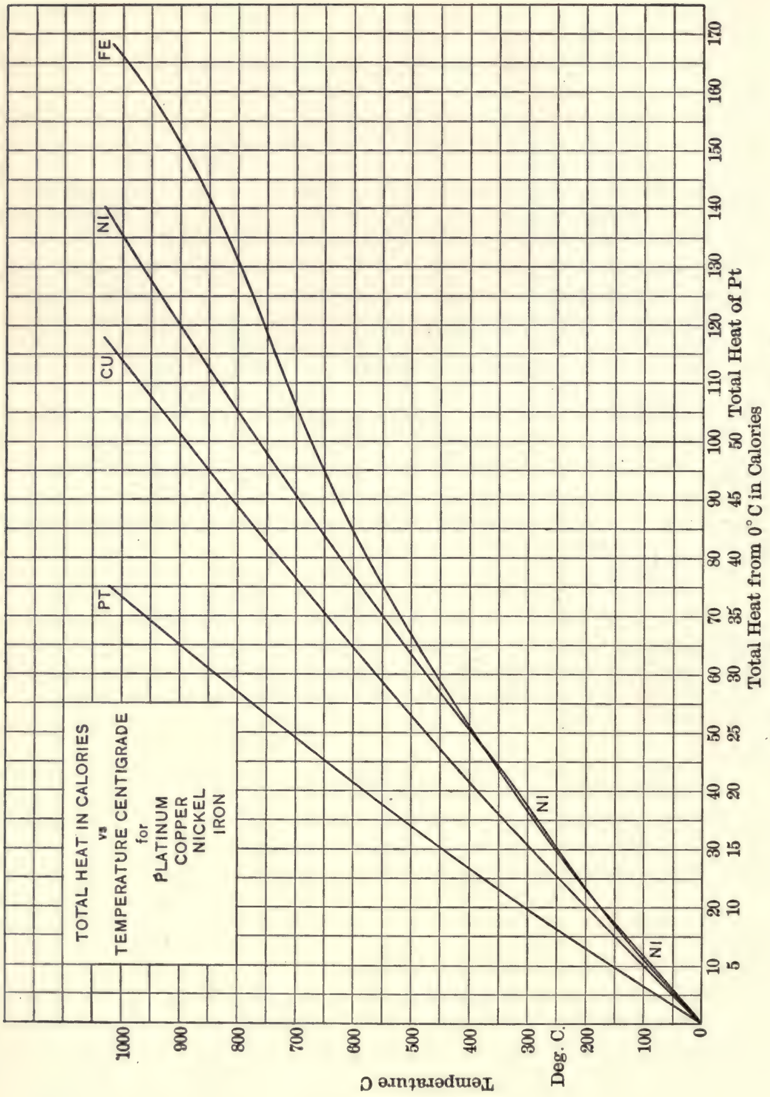


Fig. 17. Total Heat of Metals from o° C.

abscissas total heats, and to find upon this curve the point whose abscissa has the value given by the calorimetric experiment.

In Fig. 17 are given curves of temperature in terms of total heat from 0° C. for the several metals used in specific heat pyrometry. The values of the total heats are the means, for each metal, of the experimental results cited in the several tables which follow.

Choice of Metal. — Four metals have been proposed: *platinum, iron, nickel,* and *copper.*

Platinum. — This metal was first proposed by Pouillet, and taken up again by Violle. It is much to be preferred to the other metals; its total heat has been compared directly with the indications of the gas thermometer. This metal can also be reproduced identical with itself. Iridium, which commercial platinum often carries, has about the same specific heat. The high price of these substances is an obstacle to their use extensively in works; for a calorimeter of a liter it is necessary to have at least 100 grm. of platinum, — or $100 in a volume of 5 c.c., — easily lost or made away with.

Violle determined the total heat of platinum from 0° to 1200°, and computed it by extrapolation to 1800°.

W. P. White has determined the specific heat of platinum to 1500°, obtaining somewhat lower values than Violle. The differences cannot be accounted for by differences in temperature scales. A few measurements by Tilden to 600° give values between the others, and Plato at 600° and 750° finds values agreeing closely with White's.

TOTAL HEAT OF PLATINUM FROM 0° C. IN CALORIES.

Temperature.	Violle.	White.
100	3.23	....
200	6.58	....
300	9.95	9.49
400	13.64	13.09
500	17.35	16.75
600	21.18	20.44
700	25.13	24.15
800	29.20	27.88
900	33.39	31.63
1000	37.70	35.45
1100	42.13	39.32
1200	46.65	43.28
1300	(51.35)	47.26
1400	(56.14)	49.22
1500	(61.05)	55.20
1600	(66.08)	(59.26)
1700	(71.23)	(63.45)
1800	(76.50)	.....

White's measurements on mean specific heat satisfy the equation $0.0319_8 + 3.4 \cdot 10^{-6}t$.

Iron. — Regnault, in an investigation made for the Paris Gas Company, had proposed, and caused to be adopted, iron, in attributing to it a specific heat of 0.126, instead of 0.106 at 0°. He used a cube of 7 cm. sides which was thrust into the furnaces by means of long iron bars. The calorimeter was of wood and had a capacity of 4 liters.

Various observers have determined the total heat of iron; at high temperatures the accord is not perfect among the results, as shown in the following table:

TOTAL HEAT OF IRON FROM 0° C. IN CALORIES.

Temperature.	Pionchon.	Euchène.	Harker.	Oberhoffer.	Weiss and Beck.
100	11.0	11.0	....	....	....
200	22.5	23.0	23.0	23.4	23.1
300	36.8	37.0	37.0	37.5	36.1
400	51.6	52.0	51.3	52.4	49.5
500	68.2	69.5	66.9	66.0	64.4
600	87.0	84.0	83.8	84.6	81.2
700	108.4	106.0	104.1	113.4	101.0
800	135.4	131.0	127.8	135.2	124.2
900	157.2	151.5	148.0	152.1	148.5
1000	170.9	173.0	155.7	167.0	.....
1100	.....	.....	168.8	182.6	.....
1200	.....	.....	.....	199.2	.....
1300	.....	.....	.....	215.8	.....
1400	.....	.....	.....	232.4	.....
1500	.....	.....	.....	250.5	.....

The determinations of Pionchon and of Euchène are in terms of incorrect temperature scales, at least above 800° C., and although those of the other observers are in terms of approximately the same scale, the one ordinarily used to-day, this agreement is far from satisfactory. Oberhoffer's results show an abrupt change in specific heat beginning at 650°, and changes in specific heat corresponding to the allotropic forms of iron. The results of Weiss and Beck show an abrupt change in specific heat at 750°, corresponding to the magnetic transformation point. According to Oberhoffer and Meuthen, the addition of carbon to iron increases the specific heat in the proportion of 0.0011 per each 0.5 per cent carbon added, at least for the temperature range 0° to 650° C.

In spite of its common use for this purpose, this metal is not at all suitable for calorimetric use, by reason in the first place of its great oxidability. There is formed at each heating a coating of oxide which breaks off upon immersion in water, so that the mass of the metal varies from one observation to the next. Besides, iron, especially when it contains carbon, possesses changes of state accompanied during the heating by a marked absorption of heat. By cooling in water, hardening takes place, which may irregularly prevent the inverse transformations. The use of electrolytic iron is therefore preferable, since the most marked transformation and the one at the lowest temperature is thus avoided, and the oxidation is less.

Nickel. — At the Industrial Gas Congress in 1889 Le Chatelier proposed nickel, which is but slightly oxidizable up to 1000°, and which above 400° does not possess changes of state as does iron.

The total heat of nickel has been determined by Pionchon, by Euchène, and by Weiss and Beck.

The differences are due very probably in part to impurities that the nickel may contain, as well as to experimental and temperature-scale uncertainties.

TOTAL HEAT OF NICKEL FROM 0° C. IN CALORIES.

Temperature.	Pionchon.	Euchène.	Weiss and Beck.
100	11.0	12.0	....
200	22.5	24.0	23.1
300	42.0	37.0	36.2
400	52.0	50.0	50.0
500	65.5	63.5	63.2
600	78.5	75.0	76.6
700	92.5	90.0	90.0
800	107.0	103.0	104.9
900	123.0	117.5	.....
1000	138.5	134.0	.....

Copper is sometimes used, and although when pure it appears to possess no transformation regions, it oxidizes and scales very readily and cannot be used to as high temperatures as any of the other metals proposed. In the following table are given values of the total heat of copper as computed from the experiments of Le Verrier and of Frazier and Richards.

TOTAL HEAT OF COPPER FROM 0° C. IN CALORIES.

Temperature.	Le Verrier.	Frazier and J. W. Richards.
100	10.4	9.6
200	20.8	19.5
300	31.2	29.8
400	42.2	40.4
500	54.7	51.4
600	66.5	62.8
700	77.8	74.4
800	91.0	86.5
900	103.8	99.0
1000	115.6	111.7

Calorimeters. — In laboratories a platinum mass is often employed with Berthelot's calorimeter, a description of which is given in various publications on calorimetry (Fig. 18). The thermometer used for the measurement of the rise in temperature should be very sensitive, so that a rise of from 2° to 4° be sufficient in order to render negligible the cooling correction. If use is made, for instance, of a thermometer giving the hundredth of a degree, the mass of platinum should be about one-twentieth the mass of the water in the calorimeter.

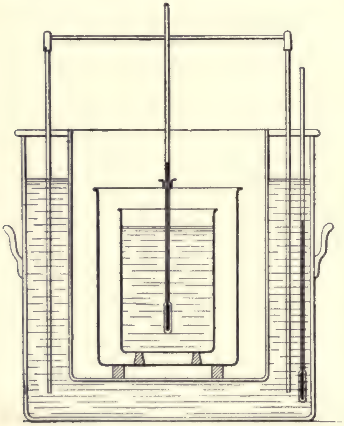


Fig. 18. Berthelot's Calorimeter.

A form of water-inclosed calorimeter, with furnace, such as used by White in specific heat determinations, is shown diagrammatically in Fig. 19. This method of operation is also applicable to temperature estimations. The water cover is swung aside when the platinum mass is dropped into the calorimeter.

This type of calorimeter is to be preferred in exact calorimetric work where high temperatures are involved, as the uncertainties of radiation and evaporation are reduced to a minimum. The usual mercury thermometer may be replaced to advantage by some form of electric thermometer.

Industrial Calorimeters (Fig. 20). — In the arts, where the measurements are made with less precision, and where it is necessary to consider the cost of installation of the apparatus, nickel may be made use of, a thermometer giving tenths of a degree, and zinc calorimeter, which may be home-made. Such an installation may cost as little as $5. A mass of nickel should be used equal to one-twentieth of the mass of water of the calorimeter.

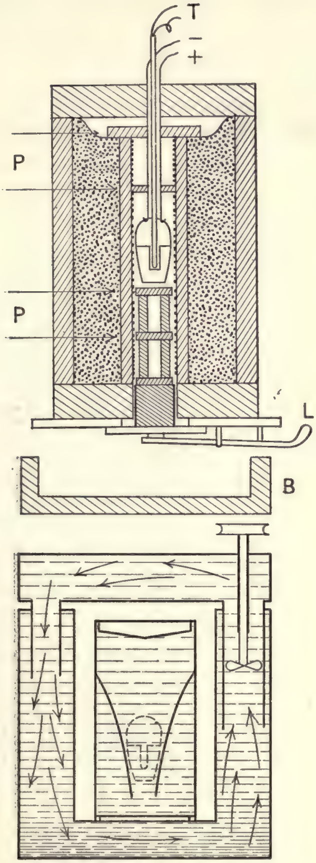


Fig. 19. White's Calorimeter.

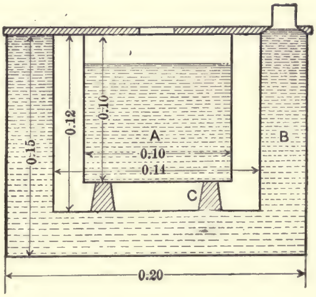


Fig. 20. Industrial Calorimeter.

The calorimeters used by the Paris Gas Company are after the Berthelot pattern; they are also water-jacketed.

Such an apparatus may consist of a cylindrical calorimeter A of two liters capacity, of zinc or of copper; a double cylindrical jacket B of the same metal, containing water, and which may be surrounded by felt on the outside. The calorimeter rests on this

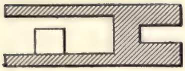


Fig. 21. Metal Carrier.

jacket by means of a wooden support C. There is preferably a metallic cover in good contact with the outside vessel. A thermometer graduated to fifths of a degree, having a small but quite long bulb, serves as stirrer. The thermometric substance is a piece of nickel of mass equal to one-tenth that of the water, or 200 grm., so as to have considerable rise of temperature easy to read by the workmen who make the measurements.

As a general rule, one must avoid placing the thermometric substance upon the floor of the furnace. The piece of nickel, which is made in the form of small cylinders having from 15 to 25 mm. diameter and from 10 to 30 mm. length, rests so as to be insulated from the floor in a nickel crucible provided with a foot and with two arms attached somewhat above the center of gravity. When it has been heated for a half-hour, an observer takes out the crucible with a forked rod, and another seizes this crucible with tongs to empty it into the calorimeter.

Use is not made of an iron crucible because this metal oxidizes and lets drop scales, which falling into the calorimeter would vitiate the experiment. Fig. 21 shows a suitable arrangement for containing a nickel cylinder.

Siemens Calorimeter. — A convenient form of direct-reading calorimeter due to Siemens is shown in Fig. 22. Using always the same mass of water and a ball of given mass and

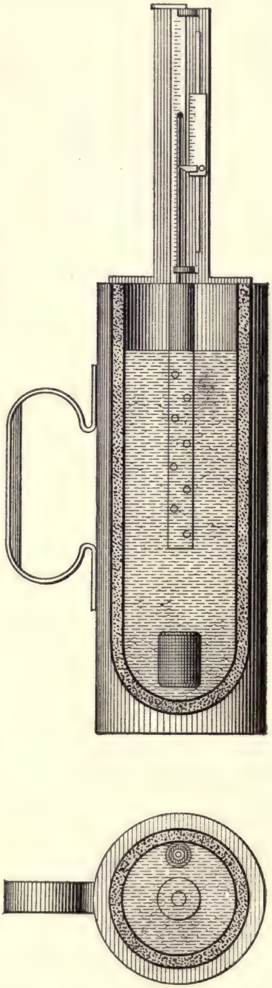


Fig. 22. Siemens Calorimeter.

kind, the thermometer or an auxiliary scale may be graduated to read directly the temperature attained by the heated ball. Hollow copper cylinders are usually furnished with this apparatus.

Precision of Measurements. — Biju-Duval made a series of experiments to study the sources of error arising from the use of the industrial calorimeter by comparing its indications to those of the thermoelectric pyrometer of Le Chatelier. The observations were taken by varying the following conditions:

Use of thermometer graduated to $\frac{1}{5}°$ or to $\frac{1}{50}°$.

Use of the old wooden gas-works calorimeter or of the water-jacketed calorimeter.

Use of iron or nickel.

I. *Experiment.* — Old wooden gas-works calorimeter. Iron. Thermometer in fifths.

$$\begin{aligned} P &= 10{,}000 \text{ grm.} \\ p &= 1031 \text{ grm.} \\ t_0 &= 20.8° \\ t_1 &= 36.2° \\ Q_0^t &= 153.5 \text{ cal.} \end{aligned}$$

Computed temperature:

Mean specific heat of iron = 0.108 $t = 1420°$
Mean specific heat of iron = 0.126 $t = 1210$
Total heat according to Biju-Duval $t = 915$
Thermoelectric pyrometer $t' = 970$

It is thus evident that the mean specific heats even with the correction suggested by Regnault give temperatures much too high. With the curve of total heats the temperature found is much too low on account of the following losses of heat:

1. Absorption of heat by the wooden walls;
2. Radiation from the iron cube during transfer;
3. Cooling of the water in the calorimeter, whose temperature exceeded by 16° the temperature of the surroundings.

The following experiments were made with the thermometer reading to $\frac{1}{50}$°; the piece of nickel was protected against radiation by a crucible. The two calorimeters were compared.

II. *Trial with the Wooden Calorimeter.*—

$T = 975°$ by the thermoelectric pyrometer
$P = 10{,}000$ grm.
$p = 145$ grm.
$t_0 = 20.21°$
$t_1 = 21.99°$
$L_0^T = 125$ cal.
$L_0^T = 131.5$ cal. from the curve at 975°.

The difference is 6.5 calories, or 5 per cent loss due to the jacket.

III. *Trial with the Water-jacketed Calorimeter.*—

$T = 985°$
$P = 2000$ grm.
$p = 48.4$ grm.
$t_0 = 18.86°$
$t_1 = 21.95°$
$L_0^T = 130$ cal.
$L_0^T = 133$ cal. from the curve at 985°.

The difference is 3 calories, or a loss of about 2 per cent only when use is made of a carefully made calorimeter and of a thermometer giving $\frac{1}{50}$°. This corresponds to an uncertainty of less than 20° in the temperatures sought. Some of this uncertainty may be due to the temperature assumed as correct in these measurements and to loss of heat during transfer. It is possible to work to better than 5° by the most refined methods, using a platinum mass. With the $\frac{1}{10}$° thermometers, necessitating a much greater rise of temperature of the water in the calorimeter, an uncertainty of 25° or more may exist. The relatively small mass of water used with a less sensitive thermometer is not necessarily a disadvantage, however, if the calorimeter is properly protected against heat loss and evaporation due to the greater temperature rise.

Conditions of Use. — The advantages of the calorimetric pyrometer are:

1. Its low net cost;
2. The ease of its use, which allows of putting it in the hands of a workman.

Its inconveniencies are:

1. The time necessary to take an observation, about a half-hour, except with the Siemens form;
2. The impossibility of taking continuous observations;
3. The impossibility of exceeding 1000° by the use of the piece of nickel;
4. The deterioration of the balls used due to oxidation.

Its use does not seem to be recommendable for laboratories, as there are continuous methods of greater accuracy readily available for such uses. In the laboratory, the calorimetric method is used ordinarily for the determination of specific heats at high temperatures rather than of these temperatures. In recent years, there have been introduced many refinements into calorimetric measurements, such as vacuum-jacketed calorimeters which nearly eliminate heat losses during the rise in temperature within the vessel; resistance thermometers and thermoelements of great sensitiveness and precision which give the rise in temperature within the calorimeter more accurately than does a mercury thermometer; electric heating and vacuum furnaces for the preheating of the sample without contamination to the desired high temperature; and many other details of manipulation and construction, for descriptions of which the reader should consult the writings of Berthelot, Louginine and Schukarew, Dickinson, Richards, White, Oberhoffer, and others.

It is possible, for instance, to keep the total error due to the calorimeter to within 1 in 10,000. These improvements are of the greatest importance for the exact determination of specific and latent heats and similar constants at high temperatures, but have little interest from the purely pyrometric point of view, since much more delicate and accurate temperature-measuring methods exist which do not involve the transfer of heat.

The calorimetric or specific heat pyrometer is to be recommended for certain operations below 1000° C. in technical works where it is required to make only occasional measurements of moderate precision; in cases where there is not the personnel sufficiently skillful to use the more precise or delicate methods; and finally, where the importance of the measurements is not such as to justify the buying of more costly instruments.

CHAPTER IV.

THERMOELECTRIC PYROMETER.

Principle. — The junction of two metals heated to a given temperature is the seat of an electromotive force which is a function of the temperature only, at least under certain conditions which we shall define further on. In a circuit including several different junctions at different temperatures, the total electromotive force is equal to their algebraic sum. In a closed circuit there is produced a current equal to the quotient of this resultant electromotive force and the total resistance.

Experiments of Becquerel, Pouillet, and Regnault. — It was Becquerel who first had the idea to profit from the discovery of Seebeck to measure high temperatures (1830). He used a platinum-palladium couple, and estimated the temperature of the flame of an alcohol lamp, finding it equal to 135°. In reality the temperature of a wire heated in a flame is not that of the gases in combustion; it is inferior to this.

The method was studied and used for the first time in a systematic manner by Pouillet; he employed an iron-platinum couple which he compared with the air thermometer previously described (page 61). In order to protect the platinum from the action of the furnace gases, he inclosed it in an iron gun barrel which constituted the second metal of the junction. Pouillet does not seem to have made applications of this method, which must have given him very discordant results.

Edm. Becquerel resumed the study of his father's couple (platinum-palladium). He was the first to remark the great importance of using in these measurements a galvanometer of high resistance. It is the electromotive force which is a function of the temperature, and it is the current strength that is measured. Ohm's law gives

$$E = RI.$$

In order to have proportionality between these quantities, E and I, it is necessary that the resistance of the circuit be invariable. That of the couple necessarily changes when it is heated; this change must then be negligible in comparison with the total resistance of the circuit.

Edm. Becquerel studied the platinum-palladium couple and made use of it as intermediary in all his measurements on fusing points, but he did not use it, properly speaking, as a pyrometer; he compared it, at the instant of observation, with an air thermometer heated to a temperature near to that which he wished to measure. He also tried to make a complete calibration of this couple, but this attempt was not successful; he did not take into account the irregularities due to the use of palladium; besides, he made use successively for this graduation of a mercury thermometer and of an air thermometer which did not agree with each other. He was led to assume for the relation between the temperature and the electromotive force a very complex expression; the formulæ which he gives contain together twelve parameters, while with the parabolic formula of Tait and Avénarius two suffice; thus

$$e = a + b\,(t - t_0) + c\,(t^2 - t_0^2),$$

which well represents the phenomenon for the couple in question to 1500°.

Regnault took up the study of Pouillet's couple, and he observed such irregularities that he condemned unreservedly the thermoelectric method. But these experiments were hardly conclusive, for he does not seem to have considered the necessity of using a high-resistance galvanometer.

Experiments of Le Chatelier and of Barus. — The thermoelectric method possesses, nevertheless, very considerable practical advantages for use in the laboratory as well as industrially, such as:

Smallness of thermoelectric substance;

Rapidity of indications;

Possibility of placing at any distance the measuring apparatus.

Le Chatelier decided to take up the study of this method, intending at the outset not to make disappear the irregularities which seemed inherent in the phenomena in question, but to study the law of these irregularities, so as to determine corrections which would permit of making use of this method, at least industrially, for approximate measurements. These investigations showed in their turn that the sources of error observed could be suppressed; the principal one, and the only serious one, came from lack of homogeneity of the metals up to that time employed.

Barus, whose work in this field dates from 1881, studied in great detail the thermoelectric measurement of high temperatures as well as the advantages and limitations of the various pyrometric methods. He was led from his researches to prefer the couple Pt, 90 Pt−10 Ir.

Iron, nickel, palladium, and their alloys were found to be unsuited for the exact measurement of high temperatures, because, heated in certain of their points, they give birth to parasite currents, sometimes relatively intense. D. Berthelot and others, however, have since used successfully in oxidizing atmospheres, thermocouples with palladium as one element.

As an example of inhomogeneity, consider the electromotive forces observed by Le Chatelier in carrying a Bunsen flame along beneath a wire of ferronickel of 1 mm. diameter and 50 cm. long; the electromotive forces are expressed in microvolts (millionths of a volt):

Distance........	0.05	0.10	0.15	0.20	0.30	0.35	0.40	0.50
E.M.F..........	−200	+250	−150	−1000	−500	−200	−50	−200

An electromotive force of 1000 microvolts is that given by the usual couples that we are going to study for a heating of 100°. With such anomalies as above there could hardly be any measurements possible.

These anomalies may sometimes be due to accidental variations in the composition of the wires, but in general there is no preëxisting heterogeneity; a physical heterogeneity due to the heating is produced. Iron and nickel, heated respectively to 750° and 380°, undergo an allotropic transformation, incompletely reversible by rapid cooling.

In the case of palladium, there may be produced, in a reducing atmosphere, phenomena of hydrogenation which change completely the nature of the metal, so that a metal initially homogeneous may become by simple heating quite heterogeneous and form a couple.

Certain metals and alloys are quite free from these faults, notably platinum and its alloys with iridium and rhodium. The irregularities previously observed are thus due to the employment of iron and palladium in all the couples tried.

A second source of error, less important, comes from the annealing. In heating a wire at the dividing point between the hardened part and the annealed part, there is developed a current whose strength varies with the kind of wire and the degree of hardness. The twisting that a wire has undergone at a point suffices to produce a hardening. A couple whose wires are hard drawn throughout a certain length will give different indications according to the point of the wire where the heating ceases. Here are results in microvolts obtained by Le Chatelier with a platinum, platinum-iridium (20 per cent Ir) couple (platinum-iridium alloy is very easily annealed):

	100°	445°
Before annealing	1100	7200
After annealing	1300	7800
Difference	200	600

We shall now study successively:

1. The choice of the couple;
2. Thermoelectric formulæ;
3. The methods of measurement;
4. The sources of error;
5. The standardization.

Choice of the Couple. — We shall first reproduce the evidence and arguments which led Le Chatelier to prefer and introduce the thermocouple of composition platinum against its alloy with 10 per cent rhodium for temperature measurements in those cases for which the thermoelectric method is preferable or convenient. We shall then give account of some of the later work of others in this domain.

In the choice of the couple, account must be taken of the electromotive force, the absence of parasite currents, and the inalterability of the metals used.

Electromotive Force. — This varies enormously from one couple to another. Below are several such electromotive forces given between 0° and 100° by metals that can be drawn into wires and opposed to pure platinum.

	Microvolts.
Iron	2100
Hard steel	1800
Silver	900
Cu + 10% Al	700
Gold	600
Pt + 10% Rh Pt + 10% Ir	500
Cu + Ag	500
Ferronickel	100
Nickel steel (5% Ni)	0
Manganese steel (13% Mn)	− 300
Cu + 20% Ni	− 600
Cu + Fe + Ni	−1200
German silver (15% Ni)	−1200
German silver (25% Ni)	−2200
Nickel	−2200
Nickel steel (35% Ni)	−2700
Nickel steel (75% Ni)	−3700

Barus studied certain alloys between 0° and 920°; he obtained the following results against platinum:

	Microvolts.
Iridium (2%)	791
Iridium (5%)	2830
Iridium (10%)	5700
Iridium (15%)	7900
Iridium (20%)	9300
Palladium (3%)	982
Palladium (10%)	9300
Nickel (2%)	3744
Nickel (5%)	7121

Here is another series made by Barus at the boiling point of sulphur with alloys of platinum containing 2, 5, and 10 per cent of another metal:

Metals.	Au	Ag	Pd	Ir	Cu	
2%	− 242	− 18	+ 711	+1384	+410	
5	− 832	−105	+ 869	+2035	+392	
10	−1225	−158	+1127	+3228	+257	
	Ni	Co	Fe	Cr	Sn	Zn
2%	+2166	+ 26	+3020	+2239	+261	+396
5	+3990	−170	+3313	+3123	+199	+ 24
10	+5095	− 41	+3962	+3583	+151	
	Al	Mn	Mo	Pb	Sb	Bi
2%	+779	+ 758	+ 263	−268	+1155	+245
5	+938	+2206	+1673	+338		
10	....	....	+ 766			

Of all these metals, the only ones to keep by reason of their high electromotive force are the alloys of platinum with iron, nickel, chromium, iridium, and rhodium. The following table gives, in microvolts, the electromotive forces of the 10 per cent alloys of these five metals up to the temperature of 1500°:

Temperatures.	Fe	Ni	Cr	Ir	Rh
100°	438	646	405	995	640
445	3,962	4,095	3,583	6,390	3,690
920	9,200	9,100	....	14,670	8,660
1500	19,900	20,200	....	26,010	15,550

Absence of Parasite Currents. — The alloy with nickel gives parasite currents of great intensity, as do all the alloys of this metal. It is the same with iron. Chromium does not seem to present the same inconvenience: it forms an alloy difficult to fuse and, for this reason, difficult to prepare. With the alloys of iridium and of rhodium there is no considerable production of parasite currents if the metals are pure and the alloys homogeneous.

There remain, then, but three metals to consider: iridium, rhodium, and chromium. Of the alloys of these metals with platinum, that of iridium is the one which hardens the most easily.

Chemical Changes. — All the alloys of platinum are slightly alterable. Those of nickel and of iron, at high temperatures, assume a slight superficial brownish tint caused by oxidation of the metal. No test has been made to see if, after a long time, this attack would reach even to the interior of the wires.

According to Le Chatelier the alloys of platinum, and platinum itself, become brittle by simply heating them long enough, especially between 1000° and 1200°; this is due without doubt to crystallization. The platinum-iridium alloy undergoes this change much more rapidly than the platinum-rhodium, and this latter more rapidly than pure platinum. It is questionable, however, if this effect, other than a slight crystallization, occurs in a strictly oxidizing atmosphere with couples containing only Pt, Rh, or Ir.

But a much more grave cause of the alteration of platinum and its alloys is the heating to high temperatures in a *reducing atmosphere.*

All the volatile metals attack platinum very rapidly, and a great number of metals are volatile. Copper, zinc, silver, antimony, nickel, cobalt, and palladium, at their points of fusion, already emit a sufficient quantity of vapor to alter rapidly the platinum wires placed in the neighborhood. These metallic vapors, that of silver and palladium excepted, can only exist in a reducing atmosphere. Among the metalloids, the vapors of phosphorus and of certain compounds of silicon are particularly dangerous. It is true that one is rarely concerned with these uncombined true metalloids, but their oxides in the presence of a reducing atmosphere are more or less completely reduced. In the case of phosphorus, it is not only necessary to shun phosphoric acid, but also acid phosphates of all the metals and the basic phosphates of the reducible oxides; thus silicon, silica, and almost all the silicates, clay included, must be avoided if a reducing atmosphere is employed.

The reducing flames in a fire-clay furnace lead little by little to the destruction of the platinum wires. It is thus indispensable to protect the couples against any reducing atmosphere by methods which will be indicated further on.

In taking account of these different considerations, — electromotive force, homogeneity, hardness, alterability by fire, — Le Chatelier was led to give the preference to the couple Pt − Pt + 10% Rh, with the possibility of replacing the rhodium by iridium and perhaps by chromium. In all cases the wires should be annealed electrically to 1400° before using.

The usual diameter of wire employed is 0.6 mm., but one of 0.4 mm. contains only half as much metal, and even for most industrial purposes is of sufficient robustness. In the laboratory there is advantage, especially on account of heat conduction, to still further reduce this diameter.

Thermoelectric Formulæ. — In spite of numerous attempts to solve the problem, it has thus far been impossible to deduce from purely theoretical grounds a satisfactory equation connecting the temperature and electromotive force of any thermoelectric couple. As we shall see, it is necessary to set up, for each type of couple, an empirical equation or a series of such equations which, sometimes within rather restricted temperature limits, represents well enough the desired relation. There is a great diversity of such formulæ, and there has been in the past a considerable amount of indiscriminate and unwarranted extrapolation of such empirical relations to temperature regions both high and low, in which the assumed formulæ do not hold. From the very common use of the thermocouple as a temperature-indicating device, this practice has caused considerable confusion in the values to be assigned to high temperatures. We shall call attention to some of the formulæ that have been used and point out their limitations both for interpolation and extrapolation.

In the construction of thermoelectric formulæ it is customary to assume a constant temperature, usually 0° C., for the cold junctions, and to further assume that the only source of E.M.F. is the hot junction. The complete expression, however, for the total E.M.F. developed in a thermoelectric circuit requires account to be taken also of (1) the Thomson effect, or the E.M.F.'s generated due to differences in temperature along a homogeneous wire; (2) the Peltier effect due to the heating of the junction of two dissimilar metals anywhere in the circuit; (3) the Becquerel effect, or the E.M.F.'s developed by physical or chemical inhomogeneity in a single wire.

The E.M.F. actually measured is the algebraic sum of all these quantities. Practically, the Thomson effect need not be taken account of separately in constructing a formula, as it is a function only of the temperature difference along the wires and of their nature.

The undesirable Peltier and Becquerel effects, the former occurring often in the measuring apparatus, and the latter mainly in the thermocouple wires, cannot be taken care of numerically in any useful thermoelectric formula, and must therefore be eliminated by the use of materials and methods free from these effects.

The following formulæ, therefore, all assume thermoelectric circuits in which the only sources of E.M.F. are due to the difference in temperature between the hot and cold junctions of the couple.

Thermoelectric Power. — By differentiating with respect to temperature the expression for the E.M.F.-temperature relation $E = f(t)$ for any couple, we get a quantity known as its thermoelectric power, $\frac{dE}{dt}$, which we may designate by H. This quantity is a convenient one with which to compare the numerical behavior at any temperature of two or more couples, or of one couple at different temperatures, as it gives the E.M.F. per degree of temperature. For some couples H is practically a linear function of t over considerable ranges of temperatures, i.e., $H = a + bt$ and is a measure of the sensibility of any type of couple. We may cite the following as illustrations:

THERMOELECTRIC POWERS OF THERMOCOUPLES.

Thermocouple.	Thermoelectric power (microvolts).	Temperature range.	Author.
Pt, 90 Pt – 10 Rh	$4.3 + 0.0088\,t$	0–1300	Le Chatelier
Pt, 90 Pt – 10 Ir	$11.3 + 0.0104\,t$	0–1000	Le Chatelier
Pt, Ni	$7.8 + 0.01325\,t$	300–1300	Burgess
Cu, Ni	$24.4 + 0.016\,t$	0–235	Pécheux
Cu, Constantan	$42.3 + 0.058\,t$	0–320	Pécheux
Pt – Fe (forged)	$2.5 + 0.0210\,t$	700–1000	Le Chatelier

It is usual to express H for a single substance in terms of lead as a standard at ordinary temperatures, but at high temperatures this becomes impracticable. The values of H for steels are of special interest in view of their use in many base-metal

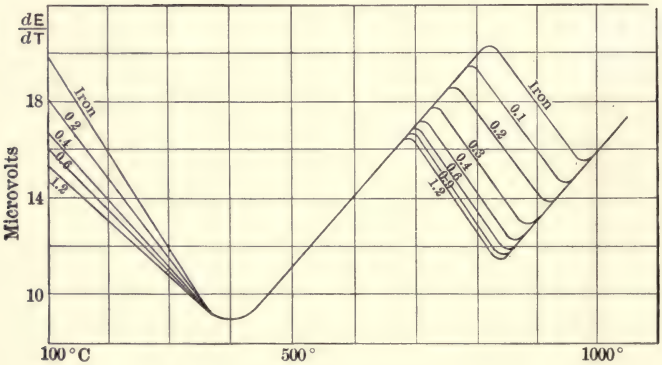


Fig. 23. Thermoelectricity of Steels.

couples. In Fig. 23, due to Belloc, are given the changes of H, with temperature and carbon content for various steels against Pt, from which it is evident that thermocouples with steel or iron as one component have complex E.M.F.-temperature relations, and that the relation between thermoelectric power and temperature is far from linear.

For some couples the thermoelectric powers of the component wires become equal and opposite in sign at some temperature known as the *neutral point*, beyond which the sign of the E.M.F. is negative. It is evidently of advantage to use couples in regions removed from their neutral point.

As shown by Stansfield, the Peltier effect $\left(T\frac{dE}{dt}\right)$ is very nearly linear with the temperature for the Pt-Rh and Pt-Ir couples, but not the thermoelectric power. Sosman's observations on various Pt-Rh couples also bear out this statement.

Formulæ. — Avenarius and Tait have shown that up to 300° the electromotive force of a great number of couples is represented in a manner sufficiently exact by means of a parabolic formula of two terms:

$$e = a\,(t - t_0) + b\,(t^2 - t_0^2).$$

The experiments of Le Chatelier on the platinum-palladium couple have shown that the same formula holds also for this couple up to the fusing point of palladium:

$$e = 4.3\,t + \frac{7.3}{1000}\,t^2.$$

t = 100	445	954	1,060	1,550
e = 500	2950	10,900	12,260	24,030

Platinum and Its Alloys. — This law fails completely, however, for couples made of pure platinum and an alloy of this metal.

Here are three early series of determinations made with different couples, giving an idea of the order of magnitude of the E.M.F.'s of thermocouples of types used very frequently, as determined by these observers.

Barus. Pt – Pt 10% Ir.		Le Chatelier. Pt – Pt 10% Rh.		Holborn and Wien. Pt – Pt 10% Rh.	
t	e	t	e	t	e
300	2,800	100	550	100	565
500	5,250	357	2,770	200	1,260
700	7,900	445	3,630	400	3,030
900	10,050	665	6,180	600	4,920
1100	13,800	1060	10,560	800	6,970
		1550	16,100	1000	9,080
		1780	18,200	1200	11,460
				1400	13,860
				1600	16,220

Holman showed that the results of Holborn and Wien may be expressed by a logarithmic formula containing only two parameters and requiring, therefore, only two calibration temperatures. Le Chatelier showed likewise that his results could also be represented by the Holman formula, and in general it may be said that for use below 1200° C. of the thermocouple made of platinum and its alloys with rhodium and iridium, the logarithmic formula satisfies the results of observations to 2° C., or well within the limits of all except the most accurate work.

Holman's formula is as follows:

$$\sum_0^t e = mt^n, \tag{1}$$

where $\sum_0^t e$ is the electromotive force of the couple for any temperature t when the cold junction is kept at zero centigrade. The two constants are readily computed or evaluated graphically, and the resulting plot serves indefinitely for the determination of any temperature with a given couple. The equation does not apply in the region in which the thermocouple is insensitive, that is, below 250° C. It may be written, for convenience in plotting and computation:

$$\log \sum_0^t e = n \log t + \log m; \tag{2}$$

so that if log e be plotted as abscissas and log t as ordinates, a straight line is obtained.

This formula has been applied successfully to the above observations of Le Chatelier on platinum-rhodium couples and to those of Barus on platinum-iridium couples.

Holborn and Day, in their very elaborate, direct comparison of the nitrogen thermometer with thermocouples made of the various platinum metals, in the interval 300° to 1100° C., found that if a precision of 1° is sought, a three-term formula is required to express the relation between E.M.F. and temperature.

The formula

$$\sum_0^t e = - a + bt + ct^2 \tag{3}$$

is the one they have used. The labor involved in computation with this form is considerable, and, unless a very great accuracy is required, Holman's formula is amply sufficient, when the uncertainty of the absolute values of high temperatures is considered.

Stansfield deduces from theoretical considerations the formula

$$T\frac{de}{dT} = aT + b, \tag{4}$$

which may be written

$$e = aT + b \log T + c, \tag{5}$$

a form which satisfies the experimental results determined with pure platinum wires. This form possesses no practical advantage over that of Holborn and Day, unless it be its usefulness, by employing the graphical method, in detecting slight errors in fusing points. The values of $\frac{de}{dT}$ at the points of fusion can be obtained from the T *vs.* e plot, and the T *vs.* $\frac{de}{dT}$ curve thus constructed throws into prominence the experimental errors at these points. As the above formulæ indicate, the curve for the platinum metals constructed with T as abscissas and $T \cdot \frac{de}{dT}$ as ordinates is a straight line. The errors of the method are less than 2° at 1000°. The ordinary metals, on the other hand, with a few exceptions such as nickel and cobalt, give nearly a straight line for the curve T *vs.* $\frac{de}{dT}$.

A formula which has been used on account of its more convenient form, than (3) for example, in the computation of temperature, is:

$$t = a + be - ce^2. \tag{6}$$

This formula satisfies the observations with platinum-rhodium and platinum-iridium couples in the range 300° to 1100° C. almost as well as (3).

We may compare these various formulæ by computing their deviations at various fixed points, making use of the latest data with comparison of a thermocouple (90 Pt · 10 Rh-Pt) with the gas-thermometer scale, — those of Day and Sosman, 1910. We shall assume as calibration temperatures for the three-term equations, (3), (5), and (6), the freezing points of zinc, antimony, and copper, and for Holman's equation (2), zinc and copper.

COMPARISON OF THERMOELECTRIC FORMULÆ
(Pt − 90 Pt · 10 Rh)

Substance.	Freezing point.	Observed (microvolts).	Observed − calculated temperatures.			
			(2)*	(3)	(5)	(6)
Cadmium	320.0°	2,502	−0.2	−0.3	+ 6.9	− 1.1
Zinc	418.2	3,429	0	0	0	0
Antimony	629.2	5,529	+2.3	0	0	− 0.1
Silver	960.0	9,111	+2.5	+ 0.2	+ 2.2	− 0.9
Gold	1062.4	10,296	+0.4	+ 0.2	0	0
Copper	1082.6	10,535	0	0	0	+ 0.1
Diopside	1391	14,231	−6	+10	−10	+19
Nickel	1452	14,969	−6	+14	−11	+28
Cobalt	1490	15,423	−7	+14	−13	+31
Palladium	1549	16,140	−5	+20	−14	+42
Platinum	1755	18,613	+1	+42	−15	+73

* The numbers in parentheses refer to formulæ on preceding pages.

It is evident from the table that we have, therefore, as many thermoelectric scales as we have equations. The two formulæ which best fit the region 300° to 1100° C., namely, (3) and (6), are clearly not suited for extrapolation without applying proper corrections. Of all the formulæ, Holman's (2), which is also the simplest, is the best suited for general use throughout the whole range 300° to 1750°, giving a maximum error of 2.5° below, and of 7° above, 1100° C. None of these equations is satisfactory for the most exact work, however. A cubic equation in *t* will satisfy the data more exactly, but this is extremely inconvenient to solve for *t*; or two parabolas of type (3) may be used, the first from 300° to 1100°, the second from 1100° to 1750°.

In 1905, Harker, using thermocouples of platinum against a 10 per cent rhodium and 10 per cent iridium alloy of platinum, respectively, and extrapolating equation (3) from 1100° C., obtained 1710° C. with both types of thermocouple as the uncorrected value of the platinum melting point. This value, 1710° C., has been generally accepted in many quarters as the true melting point of this metal. Waidner and Burgess, however, demonstrated in 1907 that the value found for high melting points by extrapolating with thermocouples depends not only on the thermoelectric relation assumed, but also on the nature of the couple. Some of their results for the palladium and platinum melting points are given below, the calibration equations and temperatures being the same as in the above.

EXTRAPOLATION WITH VARIOUS THERMOCOUPLES.

Type of couple.	Equation.	Palladium, $MP = 1549$.	Platinum, $MP = 1755$.
4 of Pt, 90 Pt − 10 Rh (approx.) 2 makers	(3)	1521° to 1537°	1698° to 1715°
	(2)	1536 to 1561	1717 to 1754
2 of Pt, 90 Pt − 10 Ir 2 makers	(3)	1525 to 1528	1705 to 1710
	(2)	1516 to 1541	1697 to 1728
2 of 90 Pt − 10 Rh, 80 Pt − 20 Rh	(3)	1507	1687 to 1710
	(2)	1531	1734 to 1755
2 of Ir, 90 Ir − 10 Ru	(3)	1533 to 1551	1704 to 1738
	(2)	1517 to 1565	1676 to 1757

It would appear from these data that the corrections to apply to a given type of thermocouple computed and extrapolated with a given formula are uncertain, the slight variations in composition of the alloy wire from one couple to another apparently producing considerable differences in the computed temperatures.

It is an interesting fact that the 10 per cent alloys of Rh and Ir with Pt, when treated by equation (3), give very exactly the same temperature scale to the melting point of platinum, although the actual shapes of the E.M.F. temperature curves are very different for those two couples, that for Pt − Ir being the more nearly linear. It was an instructive case of two negatives not making an affirmative to assign the value 1710° as the true Pt melting point because both Ir and Rh couples led to the same result.

Using Pt-Rh couples of 1, 5, 10, and 15 per cent Rh, and calibrating in terms of equation (3) at the melting points of copper, diopside, and palladium (see above), Sosman finds 1752° as a mean value for Pt with a range of only 7°.

Variation of E.M.F. with Composition. — Sosman has also studied this for the Pt-Rh couples, and some of his results are given in Fig. 24. It will be noticed that in the region of the 10 per cent alloy, which is the one most commonly met with, or at least such is the nominal composition usually given, a change of 1 per cent in composition is equivalent to about 50° at 1000°.

The Base-metal Couples. — The E.M.F.-temperature relation for some of these couples, of which there are a great many in use, is very nearly linear. For some couples, on the other hand, the E.M.F.-temperature relation is very complex; and in those cases in which there are allotropic or other transformations within the material, taking place over a temperature range or along the wire as the successive portions are heated or cooled, there sometimes occur inflections in the curve, producing regions of considerable extent in which the couple is relatively very insensitive. When such inflections occur, there is usually no conveniently expressed relation between E.M.F. and temperature (see Fig. 23). We shall call attention later to some specific cases of base-metal thermoelectric formulæ.

Methods of Measurement of Temperature. — Two methods may be used to measure the electromotive force of a couple: the method of opposition and the galvanometric method. From the scientific point of view, the first alone is rigorous; it is usually made use of in laboratories. The second method is simpler, but possesses the inconvenience of giving only indirectly the measure of the electromotive force by means of a measurement of current strength. This inconvenience is more apparent than real in the later forms of instrument, as will be shown.

There are sources of error, however, inherent in the galvanometric method, such as effects of lead resistance and temperature coefficients of leads and galvanometer, which, as we shall see, are difficult if not impossible of complete elimination even with the best apparatus available. The method of opposition, on the other hand, may be made, in so far as the measurements of E.M.F. are concerned, as exact as may be desired, or so that

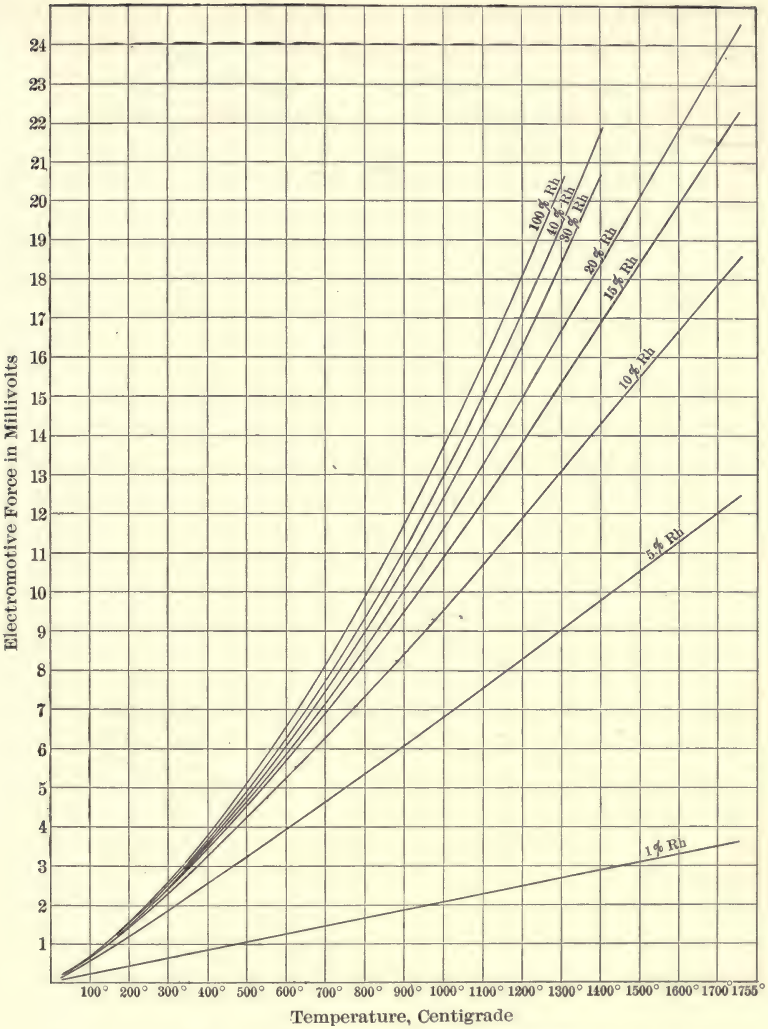


Fig. 24. E.M.F. of Pt-Rh Thermocouples.

the only outstanding uncertainties are inherent in the thermocouple itself. These uncertainties, such as inhomogeneity and conduction along the wires, variable zero, and actual change of E.M.F., are sometimes overlooked, giving rise to illusory accuracy.

We shall describe each of these methods and discuss their limitations, and also point out the sources of error most likely to be present with the various types of thermoelectric apparatus.

Galvanometric Method. — The measurement of an electromotive force may be reduced to that of a current; it suffices for that to put the couple in a circuit of known resistance, and from Ohm's law we have

$$E = \frac{I}{R} \cdot$$

If the resistance is not known, but is constant, the electromotive force will be proportional to the current strength, and that will suffice, on the condition that the calibration of the couple is made with the same resistance. If this resistance is only approximately constant, the relation of proportionality will be only approximately exact.

This method is the one used in practically all industrial practice, and to-day galvanometers can be had satisfying all the requirements of which we shall treat in the following paragraphs. In many quarters the thermoelectric pyrometer has been discredited because instruments giving evidently unreliable results were used. With a better understanding of the requirements and the meeting of them by manufacturers, this prejudice is disappearing.

Resistance of Couples and Galvanometer. — The wires of the couple make necessarily a part of the circuit in which the current strength is measured, and their resistance varies with increase of temperature. It is important to take account of the order of magnitude of this inevitable change of resistance.

Barus made a systematic series of observations on the alloys of platinum with 10 per cent of other metal. The relation between the resistance and the temperature being of the form

$$R_t = R_0 (1 + \alpha t),$$

he obtained the following results:

	Pt (pure)	Au	Ag	Pd	Ir	Cu	Ni	Fe	Cr	Sn
Specific resistance in microhms (R)	15.3	25.6	34.8	23.9	24.4	63.9	33.7	64.6	42	39
1000 α	2.2	1	0.7	1.2	1.2	0.2	0.9	0.4	0.5	0.7

Other tests gave the figures below:

	5% Al	5% Mn	10% Mo	5% Pb	2% Sb	5% Bi	2% Zn	5% Zn
R_0	22	50	17.6	7.7	29.5	16.6	47.8	25
1000 α	1.5	0.4	1.9	1.8	1	2	0.3	1.1

The coefficient α is taken between 0° and 357° (boiling point of mercury).

The experiments of Le Chatelier, for the couples that he used, gave the following results:

For platinum,

$$R = 11.2 (1 + 0.002\, t) \text{ between } 0° \text{ and } 1000°.$$

For platinum-rhodium (10% Rh),

$$R = 27 (1 + 0.0013\, t) \text{ between } 0° \text{ and } 1000°.$$

Holborn and Wien found for pure platinum,

$$R = 7.9 (1 + 0.0031\, t) \text{ between } 0° \text{ and } 100°,$$
$$R = 7.9 (1 + 0.0028\, t) \text{ between } 0° \text{ and } 1000°.$$

Very commonly couples are made of the platinum metals of wires 1 m. in length and 0.5 mm. in diameter; their resistance, which is about 2 ohms cold, is doubled at 1000°. If use is made then of a galvanometer of a resistance of 200 ohms, and if the variation of the resistance of the couple is neglected, the error is equal to $\frac{1}{100}$. In general this error is still less except in certain industrial uses. Thus in the laboratory the length heated is often less than 10 cm., and then the error reduces to $\frac{1}{1000}$.

We may calculate the effect of resistance in the electrical circuit, including that of the couple and galvanometer, on the reading of the pyrometer galvanometer in the following way: If E is the true E.M.F. generated by the thermocouple and E' the E.M.F. indicated by a galvanometer of resistance R, in series with the couple and leads, of resistance r and r' respectively, then

$$E = \frac{E'(R + r + r')}{R}.$$

In the case of certain industrial installations, where the galvanometer is at a distance from the couple, the value of r', the resistance of the copper wires connecting the couple to the galvanometer, may be of as great importance as that of the couple wires, r. The value of r' can of course be kept down, however, by increasing the size of wire used.

Although in the case of platinum couples, which on account of cost, high specific resistance, and temperature coefficient of the materials necessarily have an appreciable resistance and therefore require a relatively high resistance galvanometer, it should be noted that, with base-metal couples of large cross section and consequently low resistance, galvanometers of very much lower resistance, and therefore of a more robust type, in general, may be allowed here. For example, if the couple has a resistance of 0.1 ohm and the connecting leads a negligible resistance, as may readily happen with certain types of pyrometer rod, the galvanometer may be a millivoltmeter of only 10 ohms without introducing errors over $\frac{1}{100}$, or 10° at 1000° C., due to this cause.

Pyrometer Galvanometers. — It may still be of interest to recall the historical development of this phase of the subject, as it offers a good illustration of the influence of one field of activity on another, and from the fact that the difficulties encountered and the precautions to be taken in the construction and use of these instruments are not yet sufficiently well appreciated by some manufacturers as well as by many experimenters and other users.

The earliest measurements, those of Becquerel and of Pouillet, were made with needle galvanometers controlled by terrestrial magnetism. Such apparatus, sensible to jarring, requires delicate adjustment, and the readings take a long time. The use of these instruments would have prevented the method from becoming practical. It is only thanks to the use of movable-coil galvanometers of the Deprez-d'Arsonval type that the thermoelectric pyrometer has been able to become, as it is to-day, an apparatus in current usage.

This apparatus, in one of its earlier forms (Fig. 25), is composed of a large horseshoe magnet between whose poles is suspended a movable frame through which the current passes. The metallic wires, which serve at the same time to suspend the coil and bring in the current, undergo then a torsion which is opposed to the displacement of the coil.

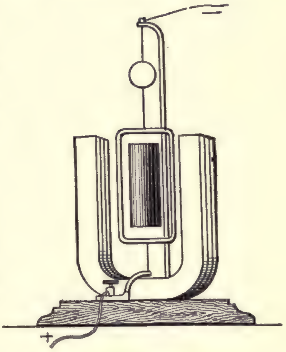


Fig. 25. Moving-coil Galvanometer.

The latter stops in a position of equilibrium which depends both on the strength of the current and the value of the torsion couple of the wires. To these two forces is added, in general, a third, due to the weight of the coil, which causes disturbing effects often very troublesome. We shall speak of this further on.

The measurement of the angular displacement of the coil is made sometimes by means of a pointer which swings over a divided scale, more often by means of a mirror which reflects on a semitransparent scale the image of a wire stretched before a small opening conveniently lighted.

These movable-coil galvanometers were for a long time considered by physicists as unsuited for any quantitative measurements; they were only employed in null methods and made accordingly. In order to render them suitable for quantitative measurements of current, it was necessary to attend to a series of details of construction, previously neglected. Here are the most important among these, as noted by Le Chatelier for suspended-coil galvanometers:

1. The *movable coil* should possess a resistance as little variable as possible with the surrounding temperature in order to avoid corrections always very uncertain. The coils of copper wire ordinarily used to augment the sensibility should be absolutely discarded; use should be made of coils of German silver or of similar metal with small temperature coefficient such as manganin.

2. The spaces which separate the coils, from the poles of the magnet, on the one hand, and from the central soft-iron core on the other, should be sufficiently great to avoid with certainty any accidental friction which would prevent the free movement of the coil. The rubbings to look out for do not come from the direct contact of the frame with the magnet: these latter are too visible to escape unseen. Those which are to be guarded against come from the rubbing of filaments of silk which stand out from insulating covering of the metallic wires, and from the ferruginous dust which clings to the magnet. It is here, it would seem, that the most serious source of error is met with in the use of the movable-coil galvanometer as measuring instrument. There is no warning indication of these slight rubbings which limit the displacement of the coil without, however, taking from it its apparent mobility.

3. The suspending wire should be as strong as may be to support the coil without being exposed to breaking by shocks; on the other hand, it should be very fine, so as not to have too great a torsion couple. Two different artifices help to reconcile somewhat these two opposed conditions: the use of the mode of suspension of Ayrton and Perry, which consists in replacing the straight wire by a spiral made of a flattened wire, or more simply the use of a straight wire flattened by a passage between rollers.

The first method offers the greatest security from shocks; it is, on the other hand, more difficultly realizable; minute precautions should be taken to prevent any rubbing between adjoining spirals. The second method allows more easily having the large angular displacements which are indispensable when it is desired to take readings upon a dial.

The most essential property necessary for the wires is absence of permanent torsion during the operations. These torsions cause changes of zero which may render worthless all the observations if account is not taken of this, which complicates matters considerably if such correction has to be made. This result is reached by using wires as long as possible, having not less than 100 mm. length, and by avoiding giving to them an initial torsion, a precaution that should be kept constantly in mind, which it often is not. When one wishes to adjust the coil to the zero of graduation, one turns often haphazard either one of the wires; it may be then that each of the wires is given an initial torsion of considerable magnitude and of opposite sign. If the two wires are not symmetrical, as is ordinarily the case, the permanent deformation resulting from this exaggerated torsion will cause a continual displacement of the zero which may last for weeks and months, increasing or decreasing during the observations according to the direction of displacement of the coil. This torsion is easy to obviate at the time of construction, but it is not possible to verify later its absence in the case of round wires or spirals except by dismounting the apparatus. On the contrary, by the use of stretched flat wires it is very easy upon simple examination to determine the existence or absence of torsion. This is another reason for employing them.

Finally, use must be made of wires having a very high elastic limit. For that it is necessary that the metal has been hardened, and besides that the metal does not undergo spontaneous hardening at ordinary temperatures. Silver, generally employed as suspension wire, is worthless. A metal, as iron, which even after annealing possesses a high elastic limit, would be perfect if it were not for its too great alterability. One cannot be sure of having uniform hardening, because the soldering of wires, indispensable to assure good contacts, anneals them throughout a certain length. German silver is the metal the most frequently used in galvanometer suspensions destined for pyrometric measurements. The alloy of platinum with 10 per cent of nickel seems preferable; after annealing it has a high elastic limit, and possesses a tenacity much higher than that of German silver. Its disadvantage is to possess a limit of elasticity twice as great, which reduces by one-half the deflections of a given cross section of wire. Phosphor bronze also gives good results.

4. *Installation of the apparatus* for the galvanometers, in which the coil is carried by two opposed *stretched* wires, necessitates special precautions.

In the first place, it should be located beyond the influence of jarrings of the ground, which render reading impossible; then it is necessary that its position remain *rigorously* fixed. If, in fact, the two extreme points of suspension of the wires are not exactly in the same vertical, and if the center of gravity of the coil is not exactly in the line of the two points of suspension, two conditions which can be never rigorously realized, the apparatus constitutes a bifilar pendulum of great sensibility. The slightest jarring suffices to provoke very considerable angular displacements of the coil. To avoid them, the apparatus should rest upon a metallic support attached to a wall of masonry. When the apparatus is placed, as is often the case, upon a wooden table resting upon an ordinary wooden floor, in order to obtain a deflection of the coil, and in consequence a displacement of the zero, it suffices to walk around the table, which causes the floor to bend slightly, or to provoke a current of air, which, in changing the hygrometric state of the legs of the table, causes it to tip somewhat.

Coils freely suspended from above have not these disadvantages.

Types of Suspended-coil Galvanometer. — A series of galvanometers have been studied especially in view of pyrometric measurements; we shall pass them rapidly in review.

For laboratory researches the usual swinging-coil galvanometer as made by Carpentier is often used in France. One must make sure that these instruments satisfy well the indispensable conditions which we have mentioned, which is not always the case when these instruments have been constructed with reference to the ordinary experiments of physics.

This laboratory apparatus, the only one which existed at the time of the first investigations of Le Chatelier, was not transportable, and could not be arranged for experiments in industrial works. It was then necessary to devise a special model of galvanometer easy to carry about and to put in place. The apparatus (Fig. 26) is composed of two parts, the galvanometer and the transparent scale with its light. The two parts are symmetrical, and, for transportation, may be fixed back to back on the same plank carrying a handle. For observations they are fastened to a wall by means of two nails driven in at a suitable distance apart. The suspension wires, in case of breakage, may be immediately replaced. They carry, soldered to their two ends, small nickel spheres, which one has only to slip on to forked pieces attached to the top and bottom of the coil, and to the supports of the apparatus, respectively. The mirror consists of a plano-convex lens, silvered on the plane face, which gives much sharper and brighter images than the ordinary small mirrors with parallel faces.

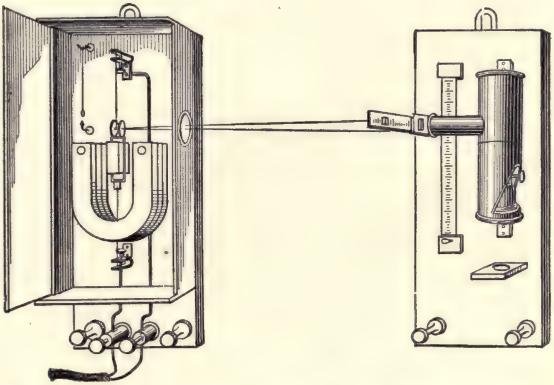


Fig. 26. Le Chatelier's Thermoelectric Galvanometer.

Carpentier has also made for the same purpose a galvanometer in which the readings are taken by means of a microscope. It is an easily transportable apparatus and very convenient. It has the fault to be subject to a displacement of the zero resulting from the unsymmetrical heating of the body of the microscope by the small lamp which lights the reticule. The stretched wires are replaced by large spirals which offer an absolute resistance to rupture by shock during transportation.

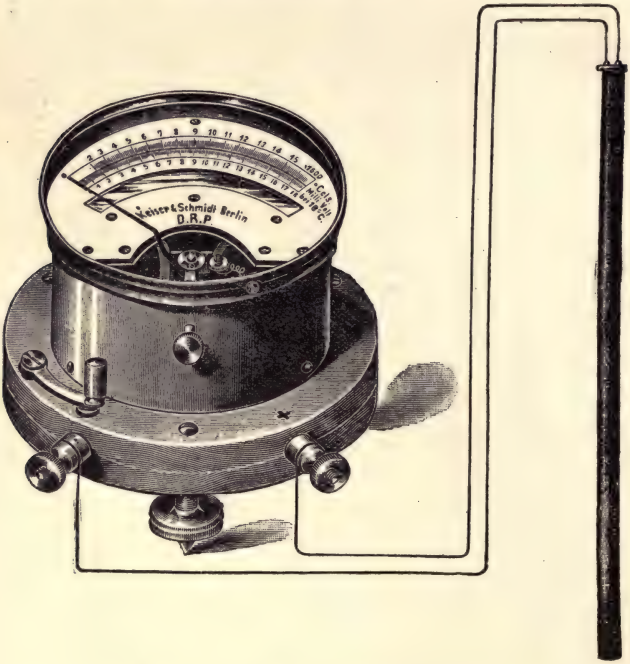


Fig. 27. Keiser and Schmidt Outfit.

The use of this apparatus necessitates an arrangement which permits, during the observations, putting the galvanometer on open circuit so as to verify the zero reading.

In the three preceding galvanometers the measurement of the deflection of the coil is made by optical means; in the following, the measurement is made by means of a needle swinging over a scale.

After a study made by Holborn and Wien at the Physikalische

Reichsanstalt in Berlin of the Le Chatelier thermoelectric pyrometer, the firm of Keiser and Schmidt devised a needle galvanometer (Fig. 27) which works fairly well, although the early forms of this instrument were of too low resistance for many industrial purposes and its temperature coefficient is unduly high. It has the disadvantage of being somewhat fragile. The suspending wire of the coil does not seem to have more than $\frac{1}{20}$ mm. diameter; the mounting of the apparatus is quite complicated. Repairs cannot readily be made either in the laboratory or works.

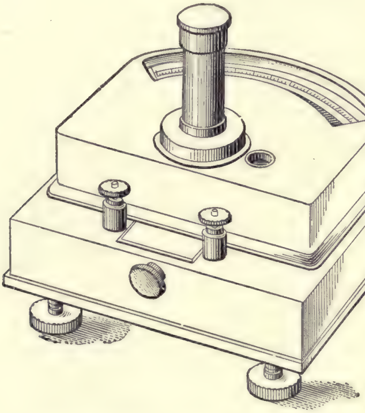


Fig. 28. Siemens and Halske Pyrometer Galvanometer.

The firm Siemens and Halske has also devised an excellent model of needle galvanometer suitable for temperature measurements (Fig. 28). Its resistance is 340 ohms, or 400 ohms in the later forms; the scale has 180 divisions, each corresponding to 10 microvolts. There is also a second graduation which gives the temperature directly with the couple sold with the apparatus. Commutators allow of putting the apparatus successively in communication with different thermoelectric couples, if it is desired to take simultaneously several sets of observations. This instrument is provided with a good level, and has a small temperature coefficient. Hartmann and Braun also manufacture excellent instruments of this type. Their wall pattern is shown in Fig. 29.

Pellin of Paris has made, from designs of Le Chatelier, a needle galvanometer of simple construction which can be repaired where it stands. The very long suspension wire is of 10 per cent nickel platinum; it has $\frac{1}{10}$ mm. diameter and is drawn out flat.

The lower wire is made of a spiral of the same wire of $\frac{1}{20}$ mm. diameter, which is situated in the interior of the iron core so as to insure uniformity of temperature. When the spirals of the suspension are unequally heated by radiation from the room or for other reason, there results considerable displacement of the zero. A spirit level permits of rendering the apparatus vertical, but it is prudent, by reason of the length of the suspension wire, to make sure directly of the absence of rubbing on the coil. For this a slight jar is given to the apparatus; the point of the needle should take up and keep for a long time a slow oscillatory movement in the direction of its length; the transverse oscillations ceasing rapidly indicate friction upon the coil.

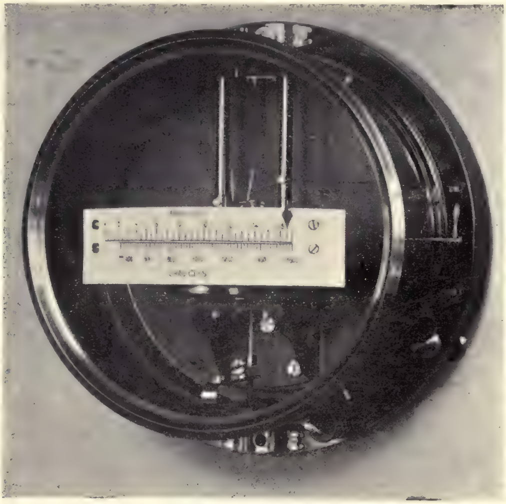


Fig. 29. Hartmann and Braun Wall Type.

√ *Pivot Galvanometers.* — The development of satisfactory pivoted moving-coil electrical instruments with spring control, whose indications as given by a pointer on a scale do not change with time, is very largely due to Weston. It is only recently, however, that pivoted millivoltmeters of sufficiently high resistance and range to use with platinum couples have been made. The characteristics of the design of one type of such instruments are shown in Fig. 30, illustrating Paul's mono-pivot construction.

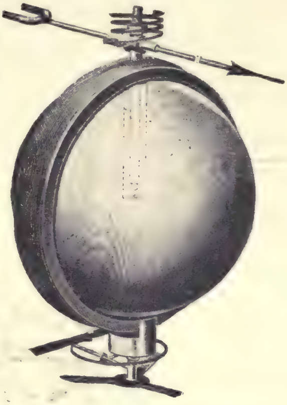


Fig. 30. Paul's Unipivot Mounting.

The indicator is a low-reading moving-coil voltmeter, the circular coil of which is pivoted at the center of a spherical iron core, and carefully balanced so that its position is unaffected by vibration or want of exact leveling. The pivot works in a finely polished jewel, from which it is completely lifted on depressing a plunger projecting through the top of the instrument, thus rendering the apparatus proof against rough handling in transit. A moving coil of low resistance is used in conjunction with a large resistance of negligible temperature coefficient included in the instrument, so that any error due to change of temperature of the indicator is thus reduced to a minimum. The movement of the coil is controlled by a spring, and the index may be set to zero, should this be necessary, without opening the instrument, an external adjustment being provided for this purpose. The unipivot principle entirely eliminates the delicate suspensions previously used, which frequently caused trouble by accidental breakage, this necessitating the entire readjustment of the apparatus.

In general, we may point out that for this type of galvanometer the case must be dust-free to avoid the collection of particles in the very small clearance of the moving coil, mounted between the pole pieces of a powerful permanent magnet. When well designed the magnetic circuit does not change its qualities appreciably in years, and such instruments are very little affected by extraneous magnetic fields, and are very robust, being capable of standing relatively rough handling. They require no leveling and several types have no adjustment whatever. It is usually well, however, to have a set screw to lock the pointer or coil system, unless, as is sometimes the case, lifting the instrument clamps the pointer. It is also convenient to be able to adjust readily the zero position of the galvanometer, and also to be able to eliminate mechanically the effects of temperature change on the readings of such an instrument. There are many millivoltmeters on the market of sufficient range and sensibility for the thermoelectric measurement of temperature, but only a very few of them are properly designed for such usage, and great care should be taken, in purchasing a pivot galvanometer, to find out if the instrument in question is suited for the work in hand. It has been the custom of some dealers in pyrometric apparatus to make use, for example, of pivot millivoltmeters of absurdly low resistance in connection with relatively high resistance thermocouples (see page 119). A millivoltmeter may, therefore, be suitable for use with one type of thermocouple and not with another.

In order to enjoy the practical conveniences of the pivot type of galvanometer, at least when using platinum thermocouples, some sacrifice of precision, range or sensibility has to be made. It appears to be as yet impracticable, for example, to make open-scale instruments with a range of 18 millivolts and increase the resistance above 170 ohms, and the range of the best makes is from 90 to 160 ohms. In this case, as we have seen, the reading of the galvanometer will depend somewhat upon the length of leads and upon the depth of immersion of the couple in the heated space.

There are a great many manufacturers of low-resistance pivot millivoltmeters, some of which are suitable for use with base-metal couples of sufficiently low resistance. Among the manufacturers of pivot instruments suitable for use with platinum couples are Paul of London, Siemens and Halske, and the Cambridge Scientific Instrument Company. The first makes a unipivot galvanometer, and the others double-pivot instruments of the Weston type.

Temperature Coefficient of Galvanometers. — It is desirable that the readings of indicating galvanometers be as little affected as possible by temperature changes in the instruments themselves. In the earlier pyrometer galvanometers this matter was generally overlooked, but in many of the newer instruments provision is made for eliminating this effect. Some of the instruments most commonly used in pyrometric practice have temperature coefficients ranging from 0.03 per cent to 0.25 per cent per degree C., depending on the type and maker. They all read too low for an increase in temperature. That this is a serious source of error is evident from an example. If an instrument having a temperature coefficient of 0.1 per cent per degree C. is calibrated at 15° C. and is used at 35° C., as may readily happen in practice, its readings will be low by 2 per cent, or 20° C. at 1000° C., due to this cause alone.

The simplest method in theory for the elimination of this effect is to use wire having no temperature coefficient, such as manganin, for the coil and auxiliary resistance of pyrometer galvanometers. Manganin has the further advantage that its Peltier effect against copper is almost zero. It appears, however, to be difficult to get sufficient sensibility in this way due to the high specific resistance of manganin.

There are various other devices for cutting down or eliminating this effect, some based on the choice of materials for and the ratio of the coil and balance resistances, and others on the variation of the strength of the magnetic field between the pole pieces, effected either by hand or automatically.

In the single-pivot indicators of 100 ohms total resistance, of R. W. Paul of London, for example, the resistance of the copper moving coil is only 10 ohms, the balance being of manganin, reducing the temperature variation in the resistance of this galvanometer to the order of 0.047 per degree C.

The use of an adjustable magnetic shunt for the elimination of this temperature correction may be illustrated as follows: The deflection D of the galvanometer may be considered proportional to the product of the flux F of the magnet by that, f, of the moving coil, or $D = kFf$. But f is directly proportional to the electromotive force e to be measured and inversely to the resistance of the circuit, whence

$$f = k' \frac{e}{r_{15}\left[1 + \alpha (t - 15)\right]},$$

where r_{15} is the resistance of the circuit at 15° C., α its temperature coefficient, and t its temperature. We have, therefore,

$$D = kk'F \frac{e}{r_{15}\left[1 + \alpha (t - 15)\right]}.$$

Since F remains sensibly constant with temperature, it follows that in order to have the same deflection for a given value of e, it is sufficient to cause F to change proportionally with the resistance of the circuit.

This is realized in practice, as in the instruments of Chauvin and Arnoux, by the use of a small bar of soft iron which may be brought nearer to or farther from the poles of the magnet, which operation produces a change in the magnetic flux through the movable coil. The motion of the iron bar is controlled by a screw whose head is graduated in degrees of temperature. The temperature of the auxiliary thermometer embedded in the galvanometer case is read and the magnet-control screw set to the indicated temperature, when the galvanometer readings are then corrected for temperature coefficient.

An automatic magnetic balancing of the increase in resistance of the galvanometer coil with temperature has been introduced into the Thwing galvanometers, as shown in Fig. 31. The coil rotates about one of its ends in a uniform field between two plane pole pieces. The two magnets that are connected in parallel by these pole pieces differ from those ordinarily used in being thin and therefore flexible. These magnets are pressed together somewhat by the long arm of a strong lever, the short arm of which rests upon a post which is part of the aluminium case. The fulcrum is a bar of invar. Changes in temperature expand or contract the aluminium part, closing or opening somewhat the gap between the poles of the magnet, and the whole may be adjusted so that the change in flux through the coil may balance its change in resistance.

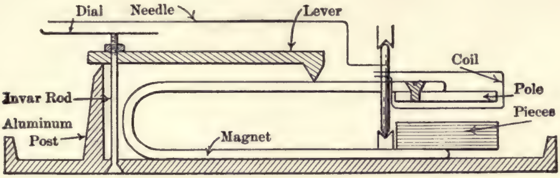


Fig. 31. Thwing's Compensating Device.

The Siemens and Halske method of temperature compensation is by a suitable combination of series and shunted resistances of copper and manganin in the swamping resistance of the instrument.

It should perhaps be emphasized at this point that the elimination of the temperature coefficient of the indicating galvanometer does not do away with making proper corrections for changes in temperature of the cold junctions of the thermocouple (see page 155).

Galvanometer Requirements for Industrial Practice. — In many industrial operations it is desirable to be sure of temperature measurements to within 10° C., often over a very considerable temperature range. This accuracy can be obtained with certain forms of the pyrometer galvanometer both with platinum couples and with some of the base-metal couples, but only when certain conditions are fulfilled by the maker and the user of the instrument. We may emphasize some of the desirable and necessary features of the galvanometer, as follows:

The instrument, if of the moving-coil pointer type, should be dust-free, of sufficient sensibility and range, and at the same time it should have an open, nearly equidistant scale which is well marked and easily read, without parallax, for example, by means of reflection of the pointer in a mirror alongside the scale. The deflection should be aperiodic or deadbeat, and the open-circuit reading should remain constant even after large deflections long maintained. There should be, in the case of suspended-coil instruments and in some pivot types, a suitable leveling device which has been accurately adjusted, and in these instruments particularly the case and other supporting parts should be free from warping. The zero position of the pointer should be readily adjustable. The instrument should either be free from errors due to changes in its temperature or else some form of compensation provided, and there should be no possibility of thermoelectric effects in the wiring within the instrument. The effects of jarring due even to shocks of considerable intensity and changes in the surrounding magnetic field should be without material influence on the readings. For pivot instruments particularly, it should be noted that the same E.M.F. always gives the same deflections. Finally, as we have before stated, the resistance of the galvanometer must be sufficiently high for the type of couple with which it is to be used. The effect of variations in the temperature of the cold ends of the thermocouple will be treated later. When a new couple is substituted, it should be noted that the E.M.F. scale of the galvanometer will still be correct, barring the effect of change in resistance of the circuit, but unless the new couple is identical in its electrical properties with the old, the temperature scale of the instrument will no longer hold.

One instrument may often serve for use with several couples of the same or of different types. It is then very important to avoid bad contacts in switches, and with very low-resistance outfits considerable errors that are not readily detectable may creep into the measurements. A galvanometer suitable for use with a Pt-Rh couple may very properly be used with a low-resistance base-metal couple of higher E.M.F. by putting additional resistance into the circuit if necessary, but a galvanometer suitable for use with the base-metal couple may be totally unfit for use with one of Pt-Rh.

The Galvanometer Method in the Laboratory. — On account apparently of its relatively low cost, and also because of its speed of operation, the galvanometer method of measuring temperatures with the thermocouple has been used frequently in scientific investigations of considerable delicacy. It should be borne in mind, however, that, even with the best pointer instruments carefully calibrated, which are much used in metallurgical and physiochemical researches, an accuracy of 5° is barely attainable with Pt-Rh couples, and this only by paying attention to the numerous sources of error we have emphasized above.

A sensitive d'Arsonval galvanometer read by reflection upon a straight graduated scale, or by means of a telescope and scale, has also been a favorite method of working. In this way the sensitiveness over the pointer method may be increased greatly, but in general the accuracy will not be very materially improved, as practically all of the troubles inherent to the galvanometer method are usually still present, whatever the method adopted for reading the deflection of the galvanometer coil. By slight modifications, the exactness of the galvanometer method may be increased, as for instance keeping the cold junctions at a definite and known high temperature and depending on the sensitive galvanometer for a smaller temperature interval; or better, by opposing the greater part of the E.M.F. of the couple with a known E.M.F. furnished by a standard cell and resistance or volt box. This last, however, is the simplest case of the potentiometric methods which we shall now study.

Potentiometric Methods. — The fundamental principle on which the many potentiometric methods are based is the adjusting of the electric circuit so that no current flows through the thermocouple. This is accomplished by balancing the E.M.F. generated in the thermocouple by an E.M.F. whose numerical value may be varied at will and measured. Since the two E.M.F.'s are in opposition, the measurements may be made to have all the advantages of a null or zero method, which is usually desirable in precision work.

Apparatus Required. — A complete installation for work to 1° C. consists of:

1. A *standard cell*, which should not have any current pass through it, and serves to determine, as term of comparison, a difference of potential between two points of a circuit through which there is a current given by an accumulator. The cell used may be a Latimer-Clark, whose electromotive force for small changes in temperature is

$$e = 1.433 \text{ volts} - 0.00119\,(t^\circ - 15^\circ).$$

This cell is made up as follows: zinc, sulphate of zinc, mercurous sulphate, mercury. The zinc sulphate should be perfectly neutral; for that, the saturated solution of the salt is heated to 40° or more with an excess of zinc oxide to saturate the free acid, is then treated with mercurous sulphate to remove the excess of zinc oxide dissolved in the sulphate, and finally crystallization is produced at 0°; one thus obtains crystals of zinc sulphate which can be immediately used.

This element is very constant. With a surface of zinc electrode equal to 100 sq. cm. and a resistance of 1000 ohms, the dropping off of the electromotive force of the cell in action does not reach $\frac{1}{1000}$; with 100 ohms only, this would be $\frac{1}{200}$. Practically it is possible, with a resistance of 1000 ohms, to limit the surface of the electrodes to 30 sq. cm., and to do away with the use of accumulators. But then the theoretical advantage of the absolute rigor of the method employed is lost.

There are other forms of standard cell which possess the advantages of portability and small temperature coefficient, rendering them better adapted for ordinary use than the original Clark form. The Carhart-Clark cell is made with unsaturated mercurous sulphate and has the E.M.F.

$$e = 1.439 - 0.00056\,(t^\circ - 15^\circ).$$

In the Weston normal cadmium cell, which has generally replaced the Clark as a standard of E.M.F., and has been officially recognized as the standard by the London Electrical Conference of 1908, cadmium and cadmium sulphate replace the zinc and zinc sulphate of the Clark cell; its E.M.F. at 20° C. is 1.0183 and its temperature coefficient to two terms as found by Wolff is:

$$E_t = E_{20} - 0.0_4406\,(t - 20^\circ) - 0.0_695\,(t - 20)^2.$$

In the portable form of the cell the cadmium sulphate is unsaturated. This portable cell has no appreciable temperature coefficient, so that no precautions as to temperature control have to be taken. This cell also recovers rapidly after maltreatment. Its E.M.F. is 1.0187 volts at 20° C., although different cells will differ slightly, i.e., by ± 0.0005 volt. Hulett has tried using a large-area cadmium cell simultaneously as a battery and standard E.M.F. with considerable success.

The values of the E.M.F.'s given above are in international volts, which are legal in the United States and used by the National Bureau of Standards, and are the values effective Jan. 1, 1911, as recommended by the International Committee on electrical standards. The values previously used for the Clark were 1.434 volts at 15° C., and for the normal Weston, 1.0189 volts at 25°, in the United States.

2. A *resistance box*, or one of the forms of potentiometer of which we shall treat immediately. The former includes a fixed resistance of about 1000 ohms and a series of resistances of 0 to 10 ohms, permitting by their combinations to realize in this interval resistances varying by tenths of an ohm. One may, for greater simplicity, but by sacrificing precision, replace this series of small resistances by a single Pouillet's rheostat having a total resistance of 10 ohms. This apparatus consists of two parallel wires of a meter in length and 3 mm. in diameter, made of an alloy of platinum and 3 per cent copper.

3. A *sensitive galvanometer* giving an appreciable deflection for 10 microvolts. Since it is placed in the circuit of the couple, and since this is a case of reduction to zero, use may be made here of a Deprez-d'Arsonval galvanometer of small resistance.

Principle of the Method. — If we have an electric circuit consisting of a standard cell, or other source of E.M.F. of known value E, and a suitable combination of resistances whose total value is R for the whole circuit; and if the thermocouple in series with a galvanometer is connected across a portion r of R so that there is no deflection of the galvanometer, the E.M.F. of the couple is given by the expression

$$e = E \cdot \frac{r}{R}.$$

A modification of this method eliminating the standard cell in actual work with the couple has its advantages. A storage cell at W (Fig. 32) is in series with a rheostat R and a series of coils or combinations of coils and bridge wire represented by AB. The E.M.F. of the standard cell at E is balanced against that of the battery W by varying R, the points of contact M and M' being at A and B and the balance indicated by no current in the galvanometer. The standard cell is now replaced at E by the couple whose E.M.F. is to be measured; M and M' are then varied in position until a balance is again obtained; then

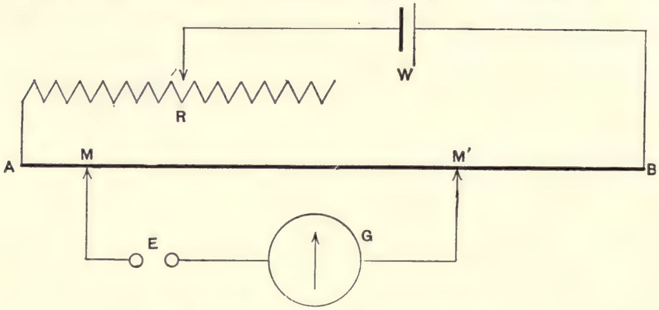


Fig. 32. Principle of Potentiometer.

$$e = E \cdot \frac{MM'}{AB}.$$

This is the simplest form of *potentiometer*, of which there are many convenient forms now available for temperature measurements.

Another modification of this method, eliminating the use of a potentiometer or carefully calibrated resistance box, but requiring a calibrated milliammeter and one or more well-known resistances, was first used by Holman in thermoelectric work, and Fig. 33 illustrates the principle. *M* is a milliammeter and *r* a small (0.1 ω) known resistance, *R* a rheostat with fine adjustment, *G* the galvanometer, and *T* the thermocouple. The deflection of *G* is brought to zero by varying *R* when the product of the current given by *M* and the resistance *r* gives the desired E.M.F. With a series of coils to substitute at *r*, the range of measurable temperature may be indefinitely extended. The precision of this method is limited by that of the milliammeter *M*. Siemens and Halske sell a convenient form of this apparatus as devised by Lindeck of the Reichsanstalt.

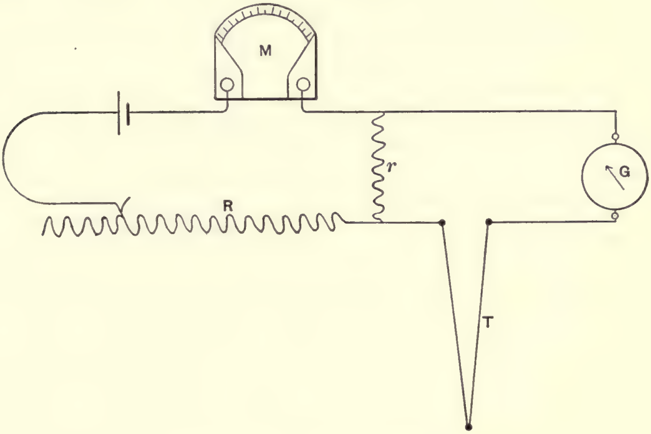


Fig. 33. Holman's Method.

Various other special forms of apparatus for the exact measurement of thermocouple E.M.F.'s have been devised, but they are all modifications, more or less complicated, of the above. We shall treat of some of them under potentiometers.

Potentiometers for Use with Thermocouples. — Although the galvanometric method is suitable for many technical thermoelectric measurements of temperature, it is generally necessary to resort to potentiometric methods when an accuracy of 10° C. or better is required, as is the case in many laboratory operations. This exact work is usually best done with thermocouples of the platinum metals, so that the problem of best design of potentiometers for temperature measurement is quite a definite one. The need of sufficiently sensitive and accurate devices for the measurement of small E.M.F.'s in thermoelectric pyrometry has acted as an incentive for the great improvement, in recent years, of apparatus suitable for this purpose, and there are now available a considerable number of potentiometers meeting the requirements for very exact temperature measurements by this method, as well as less costly instruments giving an accuracy between that obtained with the galvanometer method and the more elaborate potentiometric installations.

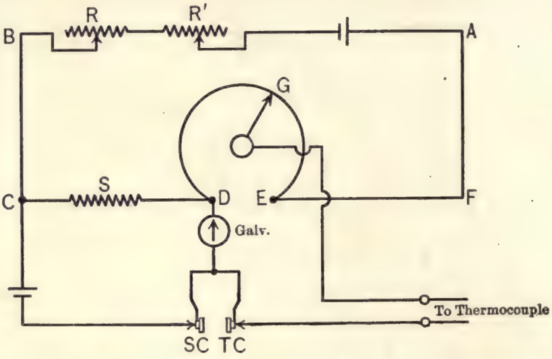


Fig. 34. Potentiometer Indicator Circuits.

The potentiometer indicator of Leeds and Northrup, shown in Fig. 34, illustrates a type of instrument of intermediate precision, but without the disadvantages of the galvanometric method, it being possible to get results to about 3° C. with this apparatus, using Pt-Rh thermocouples.

This indicator consists of a Weston standard cell, a secondary dry battery, and a galvanometer connected up as a potentiometer, the whole being mounted in a box of convenient size, making a portable testing outfit (Fig. 35). The dry cell is continuously on the closed potentiometer circuit *ABCF*, which includes the two regulating rheostats *R* and *R'* and a fixed resistance *S*. The current in the potentiometer circuit is adjusted by changing *R* and *R′* with the key at *SC* until the galvanometer shows no deflection. Pressing the key to *TC*, the pointer *G* is set on the slide wire *DE*, calibrated in millivolts, until again the galvanometer remains undeflected, indicating a balance in the thermocouple circuit.

Precision Requirements. — Some of the requirements which must be met in potentiometer construction we may emphasize. For work to 0.1° C. with Pt-Rh couples, for example, we must have a sensibility of 1 microvolt (millionth of a volt) throughout the range of the instrument, which may be of 20 millivolts, necessitating an accuracy of 1 in 20,000 in all adjustments affecting the final value of the E.M.F. Contact or thermal E.M.F.'s, such as develop even for slight temperature differences in the various parts of such an apparatus, are to be avoided in the electric circuits, as far as possible, by proper choice of materials, design, and method of manipulation; for example, using thin metal contacts, putting sliding contacts in battery circuit, and working with the galvanometer circuit closed. In order to in-

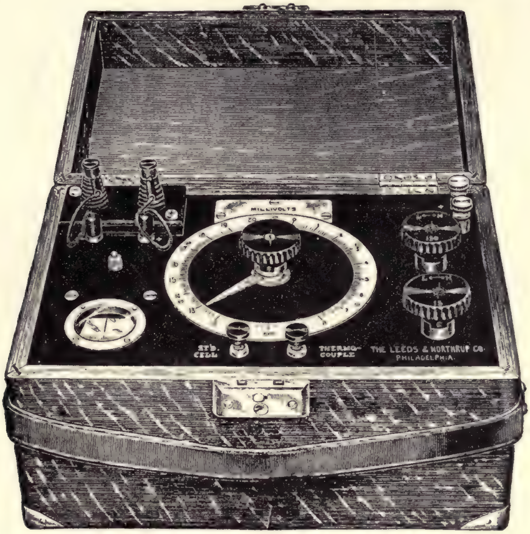


Fig. 35. Potentiometer Indicator.

crease the sensibility and permit the use of moving-coil galvanometers of reasonably attainable behavior, it is necessary to keep down the total resistance of the potentiometer. This causes the contact resistances of the adjustable parts, such as the dials, to become of importance, and a very exact and somewhat complicated mechanical construction is required to eliminate this source of error. It appears to be practically necessary, in designing a potentiometer, to choose between some contact resistance or some thermal E.M.F.

For rapid work, it is desirable that the potentiometer circuit be so designed that the standard cell may be checked up without disturbing the potentiometer circuit, and similarly it is advantageous to be able to change the range of the potentiometer without disturbing the regulating rheostats or rechecking the standard cell. Sometimes, also, the final figure in E.M.F. is obtained from the galvanometer deflection, in which case it is convenient to make provision for a constant galvanometer sensibility for all E.M.F.'s, which may be effected by auxiliary resistances in the galvanometer circuit.

A very important matter is that of insulation, or the prevention of leaks from one part of the potentiometer circuit to another (internal leakage) and from the outside to or from this circuit (external leakage). The former becomes less important with low-resistance potentiometers. The latter effect becomes particularly menacing when the thermocouple is immersed in an electrically heated furnace. It can be overcome by interposing wire-connected equipotential shields made of metal between the measuring system and all external sources of E.M.F., or by reversal of the heating or other suspected circuit and taking the mean of the potentiometer readings.

Most of the potentiometers in use are, in part at least, slide-wire instruments, but for the very highest accuracy it is advisable to use the more costly dial construction throughout. As we shall see, potentiometers suitable for the thermoelectric or resistance measurement of temperature may now be obtained, provided with five dials and reading accurately to 0.1 microvolt, or to considerably better than any thermocouple can be depended upon at high temperatures.

An inconstant battery is troublesome, and in exact work it is necessary to pay particular attention to this point in addition to frequently checking against the standard cell. Accumulators of considerable volume, or several so connected as to give a minimum change of E.M.F. with time, should be used; and it is well, since so little current is taken from the battery, to have it constantly closed through its potentiometer circuit. The battery may also be advantageously inclosed and packed to obviate temperature changes which may cause fluctuations in its E.M.F. of sufficient magnitude to be troublesome in work of high precision.

Some care has to be exercised in the choice or design of the galvanometer to be used with precision potentiometers. For work to 0.1° C. with platinum thermocouples, it is necessary to have an appreciable deflection for 1 microvolt with the galvanometer in circuit, and the design should be such that the deflection is aperiodic when the galvanometer is used with a given potentiometer. For rapid work, as in taking cooling curves, the period of the galvanometer should be kept down; and if, besides, the last increment of E.M.F. is to be measured by the galvanometer swing, it is desirable to have a period of not over five seconds. These requirements, combined with freedom from thermoelectric effects, are very severe for the swinging-coil type of galvanometer and can be met only by the more skillful constructors of such instruments.

Types of Thermocouple Potentiometer. — The Cambridge thermocouple potentiometer, similar in design to that of Harker, is an instrument designed for measuring E.M.F.'s of 30 millivolts or less. By estimation, microvolts may be read, corresponding to about 0.1° at 1000° C. with Pt-Rh couples. The circuits of this potentiometer are shown diagrammatically in Fig. 36. The total resistance in the circuit is arranged to give a fall of potential of about 1 volt per 50 ohms, and the resistances B.C. (about 42.5 ω) and S.C. (about 51 ω) are adjusted to give a fall of potential from *M* to *N* on the slide wire *ss* equal to the E.M.F. of a cadmium cell *C*.

This potentiometer is operated as follows: With *N* set at the known value of the standard cell *C*, and the key *k* thrown to *cc*, putting *C* in opposition with the storage cell *B*, the resistances R_1 and R_2 are adjusted until the galvanometer *G* shows no deflection on tapping the key. The battery *B* is then substituted for the cell *C* by throwing *k* to the side *xx* for the determination of the unknown E.M.F., *X*. The balancing of *X* against *B* is made by setting the dial, or series of millivolt coils, *MVC*, and the pointer *Q* on the slide wire *VV*, until as before the galvanometer shows no deflection on pressing the key. The value of *X* is then given directly in millivolts by adding the readings of *MVC* and *Q*. This is effected by making the dial *MVC* of 29 coils each of 0.05 ω, giving on the basis of 1 volt per 50 ohms a pressure diagram of 1 millivolt on each section. Similarly, the resistance of the wire *VV* being 0.06 ohm, the fall of potential along its length is 1.2 millivolts, or the maximum E.M.F. measurable is 30.2 millivolts. This range will take in most base-metal thermocouples as well as the usual platinum couples. In order to minimize thermal E.M.F.'s and temperature coefficients, all coils are of manganin and all connections of copper.

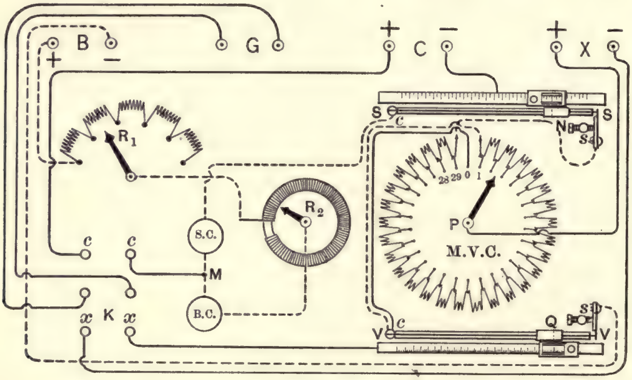


Fig. 36. Cambridge Thermocouple Potentiometer.

The Leeds and Northrup thermocouple potentiometer represents another, if somewhat similar, solution of this problem to about the same degree of accuracy. The arrangement of circuits is shown in Fig. 37. By means of the plug at *A* the range of the instrument may be increased tenfold. The heavy slide wire possesses eleven turns and permits reading to better than 1 microvolt with a suitable galvanometer. The resistance of each of the seventeen millivolt coils is 0.5 ohm, giving with the slide wire a total of about 9 ohms in the main circuit.

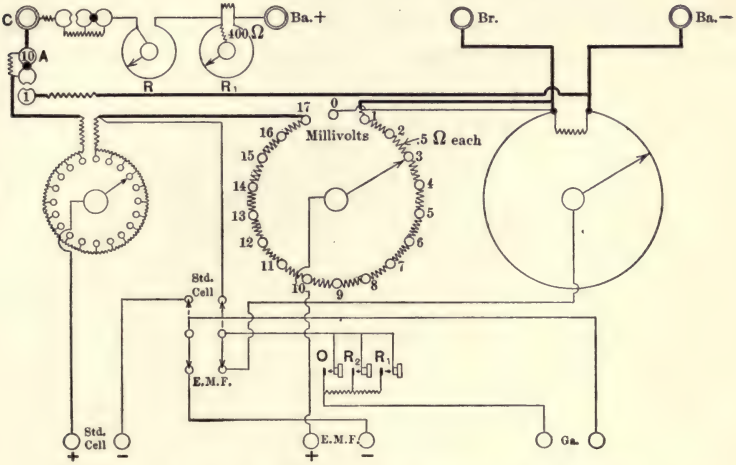


Fig. 37. Leeds and Northrup Thermocouple Potentiometer.

In both of the above instruments, settings on the standard cell may be made without disturbing the battery circuit, and the range and sensibility of either may be increased at will by suitable devices which may conveniently be built into the instruments. There are also numerous other potentiometers, such as those of Siemens and Halske, Carpentier, and Wolff, based on similar methods of operation. This type of instrument is not entirely free from internal thermoelectric forces, but these may be practically eliminated by proper reversals in the circuits.

The Diesselhorst potentiometer, built by O. Wolff of Berlin, is based on quite different principles from the preceding and represents an attempt to attain the highest accuracy possible in such apparatus, 0.1 microvolt being measurable with exactness. It is a five-dial instrument of very low resistance, and combines principles of construction suggested by several writers including Hausrath, White, and Diesselhorst. Thermoelectric effects in the main potentiometer circuit are eliminated by the design of the instrument, and temperature coefficient changes in the coils may be avoided by oil immersion. The effects of contact resistances are eliminated only by the excellence of construction. As constructed, this potentiometer possesses the disadvantages usually common to split-circuit instruments in which the range is altered by changing the battery current, such as requiring the adjustment of the rheostat in the battery circuit and rebalancing against the standard cell whenever the range of the instrument is changed. This is prohibitive for the rapid intercomparison of considerably different E.M.F.'s such as is often required in temperature measurements, unless sensibility is sacrificed.

White has developed a dial potentiometer suitable for thermoelectric work of high accuracy, in which, however, the last two dials are replaced by the galvanometer deflection, necessitating a construction, which has been realized, giving constant galvanometer sensibility. White has also realized a double potentiometer permitting alternate and independent measurements of two rapidly varying E.M.F.'s with all the advantages of two instruments, but with the accessories of only one.

Finally, Wenner has suggested a modification of the potentiometer circuit suitable for the measurement of low E.M.F.'s, consisting in shunting by a comparatively high resistance a part of the circuit including the potential point of a dial. By means of a double-dial switch both branch points between the shunt and the main circuit may be shifted in steps of equal resistance so as to introduce a larger or smaller resistance in the dial while keeping the resistance shunted constant.

In Fig. 38 is shown a plan for this potentiometer for use with thermocouples.

The dial contacts are all in the battery circuit, each branch of which is of comparatively high resistance, so that the resistance of the contacts and thermoelectromotive forces due to the setting of the dials have only a very small effect. The compensation circuit, on the other hand, is of low and nearly constant resistance, which makes it possible to use a galvanometer having a high voltage sensibility and permits the reading of a small unbalanced electromotive force from the deflection of the galvanometer (*G*).

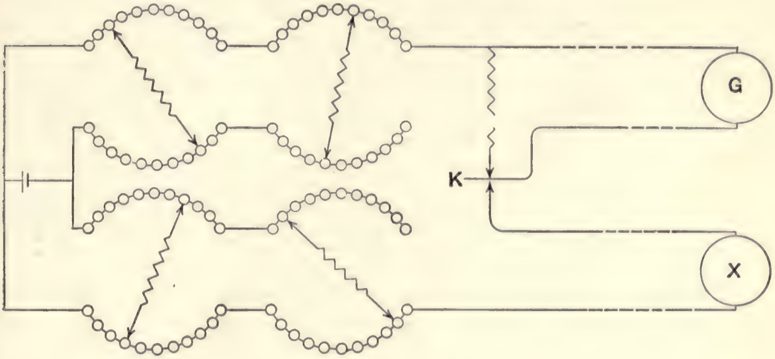


Fig. 38. Wenner's Design.

The effect of thermoelectromotive forces in the galvanometer is much reduced by keeping the circuit closed and the resistance approximately independent of the position of the galvanometer key. Under these conditions a change in the deflection of the galvanometer following a change in the position of the key (*K*) signifies an uncompensated electromotive force independent of any fairly constant electromotive force in the galvanometer.

The question of best design of precision potentiometers for use with thermocouples may be said to be in a state of flux, and no single best instrument meeting satisfactorily all the conditions imposed above has yet appeared in practical form.

The Thermocouple Circuit. — For good working of the platinum thermocouple there are certain practical precautions to be taken, which we shall consider. Most of these remarks apply even with greater force to the base-metal couples.

Junction of the Wires. — The contacts of the different parts of the circuit should be assured in a positive manner; the best way is to *solder* them. Binding screws often work loose in time, or the metallic surfaces in contact become oxidized. The importance of this precaution varies with the conditions of the experiments; one can dispense with it for experiments that last only a few hours, because there is little chance that the contacts will become modified in so short a time; soldering is, on the contrary, indispensable in an industrial installation which may be used for months without being tested anew.

But in any case, the soldering together of the two leads of the couple is absolutely indispensable. It is quite true that the electromotive force is independent of the manner of making contact. The two wires twisted together or soldered will give at the same temperature the same electromotive force. But under the action of heat the twisted parts are soon loosened, and there result bad contacts which increase the resistance of the whole circuit. In general, this accident is not noticed until the untying is almost complete, so that one may make before this a whole series of false measurements without being warned.

The best method of soldering is the autogène junction by direct fusion of the wires of the couple; it is necessary, in order to effect this, to have oxygen at hand. One commences by twisting the two leads together for a length of about 5 mm., and they are then clamped above an oxyhydrogen blast lamp. Oxygen is admitted through the central tube, and gas through the annular space; the oxygen is allowed to flow in normal quantity, and the gas in feeble quantity, then one opens progressively the gas cock. At a certain instant one sees the extremities of the wires melt, giving off sparks; the gas is then shut off. If one waits too long, the junction will melt completely and the two wires separate. With a little practice a good junction can be made by touching together, in the oxyhydrogen blast, the two untwisted wires held in the hand.

In default of oxygen, the wires may be soldered with palladium, which can be melted by means of a blast lamp furnished with air, taking care to reduce the action of radiation. A hole is cut in a piece of charcoal in which is placed the junction of the two wires twisted together after having wound about it a wire or a small strip of palladium, and the flame of the lamp is then directed upon the junction.

In the cases in which the couple is not to be used above 1000°, and only in these cases, the soldering may be done still more simply by the use of gold; the ordinary Bunsen flame is sufficient to make this junction.

Annealing. — Before use, even with new couples which are usually hard-drawn, the wires of the couple should be rendered as homogeneous as possible by annealing them electrically. For the platinum couples of 0.6 mm. diameter, which are in common use, a current of 14 amperes usually suffices. The current is kept on until the wires glow uniformly. In the case of couples that have been used, bad spots are easily detected in this way, and should be cut out if the glowing does not remove them.

Insulation and Protection. — The two leads should be insulated from one another throughout their length. For this, use may be made in the laboratory of glass tubes or pipestems, or of thread of pure asbestos wound about the two wires, by crossing it each time between the two (Fig. 60) so as to make a double knot in the form of an eight, each of the wires passing through one of the loops of the eight. This is a convenient method of insulation for laboratory use, although ordinary asbestos is likely to contain impurities which will damage the couple. The two wires with their envelope form a small rod of considerable rigidity which is easily slipped into apparatus. With this arrangement it is impossible to go above 1200° or 1300°, at which temperature asbestos melts. The most satisfactory insulation, however, is had by means of thin tubes of hard porcelain standing 1500° C. and of Marquardt mixture, 1600°, obtained from the Royal Berlin Porcelain Works.

For industrial installations, use may be made of small fire-clay cylinders of 100 mm. in length and 10 mm. in diameter, pierced in the direction of the axis by two holes of 1 mm. diameter, through which pass the wires, or hard porcelain tubes may be used. One or another of the other forms of insulator is added in sufficient numbers. They are placed, according to the case, in an iron tube or in a porcelain tube. The porcelain tube should be employed in fixed installations in which the temperatures may exceed 800°. One may, as does Parvillée in his porcelain furnaces (Fig. 39), place the porcelain tube in the lining of the furnace in such a way that its end is flush with the inner surface of the lining. An open space of a decimeter cube is cut in the lining about this extremity of the tube. This method makes easier the establishment of temperature equilibrium without subjecting the tube to too great chances of breaking by accidental blows.

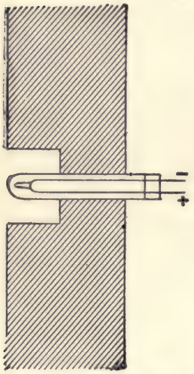


Fig. 39. Parvillée's Mounting.

The iron tube is used for temperatures not exceeding 800°, in the lead baths serving to harden steel for example, and for movable couples which are exposed to heat only during the time necessary to take the observations. In this case the junction is placed some 5 cm. beyond the insulators and the iron jacket. The wires take up the temperature within 5 seconds, and the observation can be taken before the tube becomes hot enough to be burned, even in furnaces for steel whose temperatures exceed 1600°, and before the wires have had time to be altered even in strongly reducing flames. The other extremity of the iron tube carries a wooden handle (Fig. 40) where are located, outside, the binding posts for the galvanometer leads, and inside an extra length of wire for the couple to replace portions burned or broken off. The figure shows one arrangement of this handle.

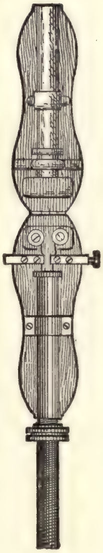


Fig. 40. Opened Wooden Handle.

In all cases in which the furnace whose temperature it is desired to measure is under a reduced pressure, suitable precautions must be taken to prevent any permanent entrance of cold air by the orifice necessary for the introduction of the tube, as well before as during an observation; otherwise one runs the chance of having inexact results.

In the case of prolonged observations in a reducing atmosphere or in contact with melted bodies, as the metals capable of altering the platinum, the couple should be protected by inclosing it in a covering impermeable to the melted metals and to vapors. For fixed installations in industrial works, use should be made of a porcelain tube, or one of iron, closed at the extremity where the junction is located; in this case the dimensions of the tube are unimportant. Quartz or porcelain tubes with an iron tube furnish oftentimes a very permanent and satisfactory sheathing. Fig. 41 shows one form of mounting for a protected couple attached to its galvanometer. For laboratory investigations it is often indispensable, on the contrary, to have around the wires a covering of as small diameter as possible. If it is simply a question of protecting the couple against the action of non-volatile metals, the simplest way is to use, as did Roberts-Austen, a paste sold in England under the name of Purimachos, which serves to repair the cazettes employed in molding. We

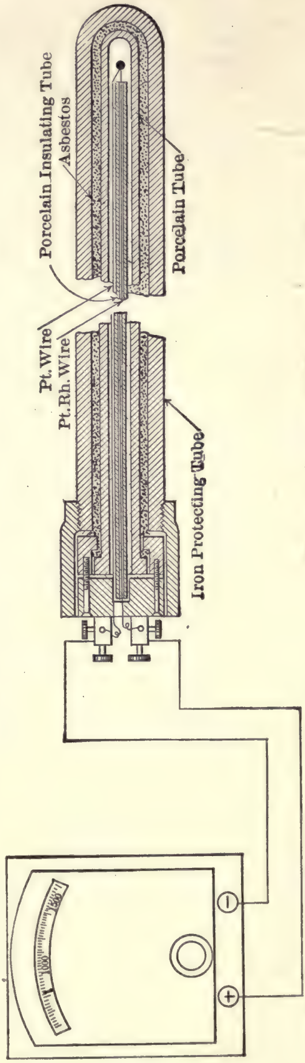


Fig. 41. Industrial Thermocouple Mounting.

have made an analysis of this which gave the following composition after desiccation at 200°:

Alumina and iron	14
Soda	3.2
Water	2.6
Silica (by difference)	80.2

It is a very finely powdered quartz to which is added 10 per cent of clay, and diluted with a solution of silicate of sodium. To use it, the matter is diluted so as to form a thick paste, and the couple is dipped in it the required length, arranging the wires parallel to each other at a distance apart of about 1 mm.

The whole may then be dried and calcined very rapidly, without fear of snapping the covering, as would happen with clay alone; but this covering is not sufficiently impermeable to protect the couple against the very volatile metals, as zinc. It is better, in this case, to use small porcelain tubes of 5 mm. inside diameter, 1 mm. thickness of wall, and 100 mm. long, straight or curved, according to the usage to which they are to be put.

The couple insulated by asbestos thread, or by a small inner porcelain tube of 1 mm. inside diameter, as has been said previously, is pushed down to the bottom of the tube. If one has not at hand such tubes of porcelain, and it is required to make a single observation at a temperature not exceeding 1000°, as, for instance, a standardization in boiling zinc, one may use a glass tube. It melts and sticks to the asbestos, which holds a thick enough layer to itself to protect the platinum. But, on cooling, the tube breaks, and it is necessary to make a new set-up for each operation. This is not practicable for continuous observations.

Fused quartz is now obtainable for insulating thermocouples and for containing sheaths. This material gradually crystallizes and crumbles above 1200°, and in the presence of a volatile reducing agent, as graphite or hydrogen, volatile silicides are formed above 1200° C., which will destroy platinum. Some types of industrial mountings used by Heræus for platinum thermocouples are shown in Fig. 42.

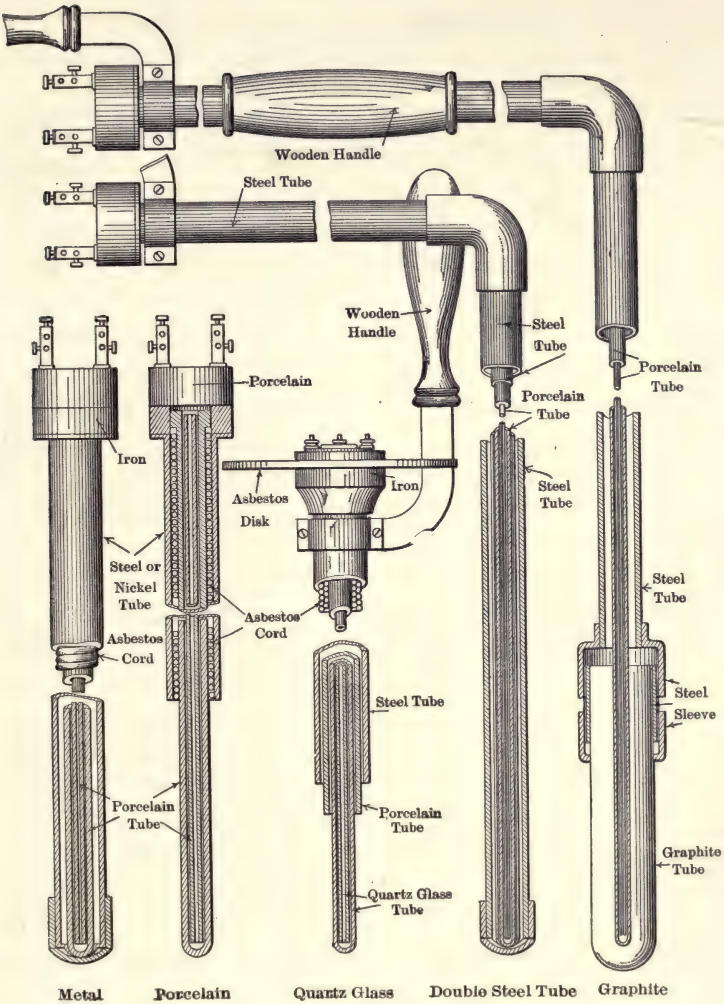


Fig. 42. Heræus' Thermocouple Mountings.

Cold Junction. — In general, in a thermoelectric element, one distinguishes the hot junction and the cold junction. The latter is supposed kept at a constant temperature. In order to realize rigorously this arrangement, three wires are necessary, two of platinum and one of an alloy connecting two junctions. This theoretical arrangement is practically without interest, and the second junction is always dispensed with. If, in fact, the temperature of the whole circuit exclusive of the hot junction is uniform, the presence or the absence of the cold junction does not affect the electromotive force; if this temperature is not uniform, the second junction is not advantageous, for there is then in the circuit an infinity of other junctions just as important to consider: the junctions of the copper leads with the platinum wires, those of the galvanometer leads and of the different parts of the galvanometer among themselves.

One must satisfy himself as well as may be as to the uniformity of temperature in the cold circuit, and rigorously of the equality of temperature between corresponding junctions, particularly those of the two platinum wires with the copper leads. These uncertainties in the temperature of the cold junctions are an important source of error in the measurement of temperatures by thermoelectric couples, but for ordinary practice they are easily eliminated. In order to realize exact measurements, precise to 1°, for instance by the galvanometer method, it will be necessary to have completely homogeneous circuits, including the galvanometer, with the single exception of the junctions of the platinum wires with the conducting leads; these should be immersed in the same bath at constant temperature. It would be necessary for this that the constructors of galvanometers limit themselves to the use of the same kind of wire for all parts of the apparatus, wires of the coil, suspending wires, leads, and parts of the coil. That is difficult to obtain.

In the standardization of thermocouples for exact work, it is customary to immerse the cold junctions, i.e., the points of contact of the copper leads and platinum-metal wires, in an oil bath in ice. With the potentiometer, irregularities due to other sources of E.M.F. in the circuit are eliminated by reversing simultaneously the battery current and the couple circuit.

The Cold-junction Correction. — In work of high accuracy with platinum couples and when the potentiometric method of measurement is used, the cold-junction correction should be experimentally eliminated by keeping the cold junctions at a constant temperature, most conveniently at 0° C.

When the galvanometer method is used, it is often not convenient to keep the junctions of the couple to the lead wires of the galvanometer at a definite temperature, although the galvanometer itself may be so removed from the furnace that its temperature changes are slight. Except in the roughest kind of work, allowance has to be made for the cold-junction temperatures, which may be measured by an auxiliary thermometer.

Calling t_0 the cold-junction temperature for which the instrument reads correctly, t the observed temperature of the cold junction, the correction to apply to the observed temperature readings of the galvanometer, otherwise supposed to read correctly for a given thermocouple, usually lies between $\frac{1}{3}(t - t_0)$ and $(t - t_0)$, depending on the type of couple and the temperatures of both hot and cold junctions. This question has been treated in detail for several types of couple by C. Otterhaus and E. H. Fischer.

That this correction depends in general upon both hot and cold junctions is due to the fact that the E.M.F.-temperature curve is not a straight line (see Fig. 24). The correction factor by which to multiply $(t - t_0)$ is numerically equal to the ratio of the tangents of this curve for the hot- and cold-junction temperatures.

As an example, we may compute the corrections to apply for a Pt, 90 Pt-10 Rh Heræus thermocouple using the E.M.F. data of Day and Sosman (page 114).

CORRECTIONS FOR COLD JUNCTION (Pt, 90 Pt-10 Rh).

Temperature of hot junction.	Correction factor for cold junctions near:		
	0°	20°	40°
100° C.	0.76	0.81	0.86
200	.65	.68	.73
300	.60	.63	.68
400	.57	.61	.65
500	.55	.59	.63
600	.54	.57	.61
700	.53	.55	.59
800	.51	.54	.57
900	.49	.52	.55
1000	.48	.50	.53
1200	.46	.49	.51
1400	.45	.48	.50
1600	.45	.48	.50

It is to be kept in mind that the E.M.F. indicated by a direct-reading galvanometer is a measure of the difference in temperature between the hot and cold junctions. If the galvanometer needle be set at zero, which is a convenient way of working, this zero reading will correspond to the temperature of the cold junction at the start; therefore the true temperature is obtained by adding to the observed temperature reading a quantity corresponding in millivolts to the cold-junction temperature, obtained as already explained. The starting point t_0 in the above is of course the temperature at which the cold junctions were kept during the original calibration, often 0° or 20° C.

Thus, if the cold junction is at 25° C. and the hot at 500°, this correction, from the above table, is $+0.60\,(25 - 0) = +15°$, if the couple was calibrated from 0° C., and the galvanometer read zero for a cold-junction temperature of 25°.

It is a simple procedure, and usually sufficiently exact when the temperature scale of the galvanometer corresponds approximately to that given by the thermocouple, to set the pointer of the galvanometer at the position on its scale corresponding to the temperature of the cold junctions. The readings of the galvanometer, otherwise corrected, will then give temperatures.

Elimination of Cold-junction Changes. — The Bristol base-metal thermocouples are provided with extension pieces of the same composition as the fire end, permitting the cold junction to be removed to a place of slight temperature change, as near the floor, and this arrangement also facilitates the convenient renewal of the short, heavy fire ends of these couples when they have to be discarded.

Bristol has also devised an automatic compensator for cold-end temperatures, shown in Fig. 43, consisting of a small glass bulb and capillary tube partially filled with mercury, into which a short loop of fine platinum wire dips. This is inserted in the thermoelectric circuit close to the cold junction. Changes in temperature cause the mercury to expand or contract, cutting in or out resistance in the circuit. This acts in opposition to the change in E.M.F. with temperature at the cold end, so that a balance may be established if the parts are properly designed.

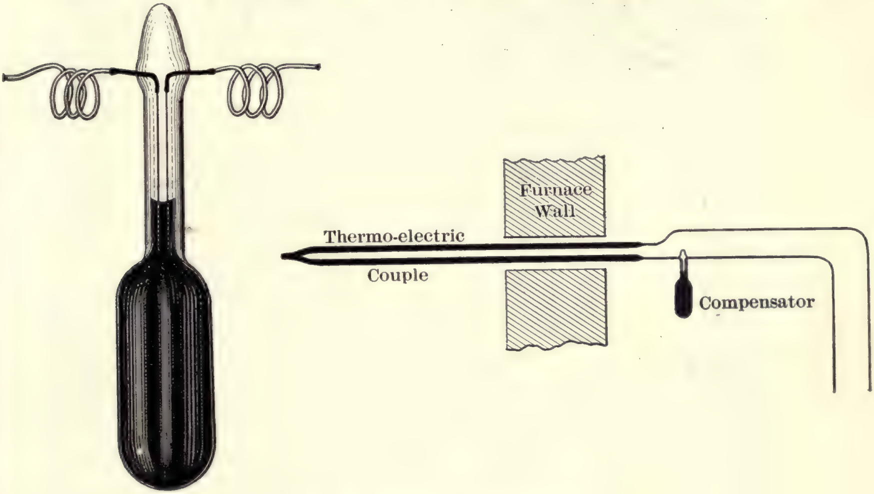


Fig. 43. Bristol's Compensator.

In the Thwing instruments, the elimination of the temperature variations of the cold ends of the couple, where they can be brought close to the galvanometer, is affected by a device consisting of a compound strip of two metals having unequal coefficients of expansion, so attached to the spring controlling the pointer that the reading of the galvanometer when no current is flowing is the temperature of the surroundings.

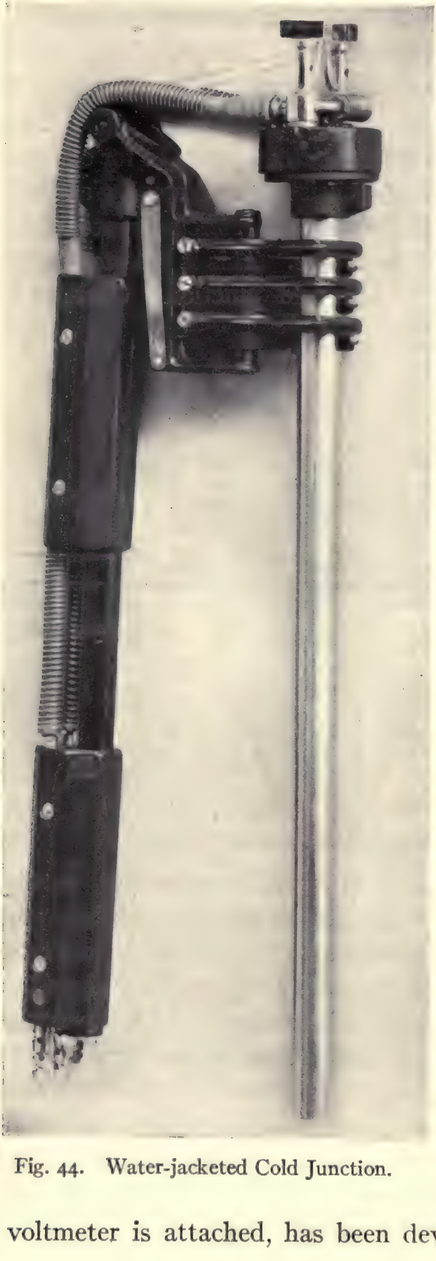


Fig. 44. Water-jacketed Cold Junction.

In many industrial establishments running water of practically constant temperature is available, and the cold end of the thermocouple can then be water-jacketed and so kept sufficiently constant in temperature, as shown in Fig. 44, which represents an arrangement for this purpose as constructed by Hartmann and Braun. The movable arm can be swung out horizontally when the thermocouple is to be immersed.

Paul provides an attachment by which an inexpensive supplementary couple, with one end water-cooled, is placed in series with and in opposition to the main thermocouple by means of nonreversible plugs which fit into sockets in the head of the pyrometer cane. The temperature difference then indicated by the instrument is that between the fire end and water-cooled end.

A Breguet spiral, to which one end of the control spring of the millivoltmeter is attached, has been devised by C. R. Darling and sold by Paul. In this way the zero of the instrument is made to vary with its temperature.

The Crompton Company provide their instruments with a multiple scale (Fig. 45), which allows for the cold-junction temperature variations.

Finally, the cold end of the thermocouple may be buried in a box underground, for instance, and copper wires run to the galvanometer. We shall mention other such devices under the heading "Compound Thermocouples" and when discussing accessories to recorders.

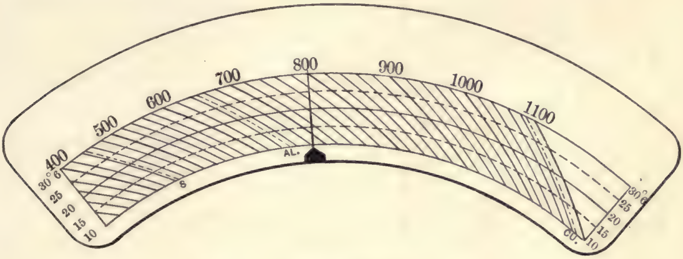


Fig. 45. The Crompton Scale.

Constancy of Thermocouples. — This matter is of the greatest importance in thermoelectric measurements both in the laboratory and in the works, as there is nothing more aggravating than the gradual deterioration of a product due to insidious, and often unnoticed until too late, changes in the controlling apparatus.

The behavior of thermocouples made of platinum and its alloys has been studied in great detail, from this point of view, by several observers, but the data are somewhat contradictory.

If a thermocouple, however well protected, is heated for a long time at a high temperature, its E.M.F. will change. It is well for accurate work to have at least two thermocouples, one of which is kept as a standard and only occasionally heated, and never above 1200° C. In this way changes in the couple ordinarily used may be readily detected. Holborn, with Henning and Austin, has made a very complete study of the effects of continued heating in various atmospheres on the loss of weight and changes produced in electric and thermoelectric properties of the platinum metals. The following table shows the results of continued heating in air on the E.M.F. of the platinum couples ordinarily used:

EFFECT OF PROLONGED HEATING ON E.M.F.
E.M.F. AGAINST PT IN MICROVOLTS.

Duration of heating, hours.	90 Pt – 10 Ir.			
	700° C.	900°	1100°	1300°
0	....	......	16,540	19,740
3	9460	12,450	15,450	18,530
6	9160	11,930	14,780	17,640
8	8840	11,560	14,300	17,050
	90 Pt – 10 Rh.			
	800° C.	900°	1000°	1100°
0	7230	8340	9480	10,670
3	7250	8380	9510	10,690
6	7270	8400	9540	......
9	7280	8410	9540	10,720
12	7290	8420	9550	......

This investigation shows that the E.M.F. of a couple, and thus the indicated temperature, changes with continued heating, very considerably for a Pt-Ir couple and about 0.5 per cent for a Pt-Rh couple for ten hours' heating. The change is greatest during the first part of the heating. The observed increase in E.M.F. of the Pt-Rh is difficult to explain unless it be due to distillation of iridium from the heating coil, as shown from Day and Sosman's work. Before use, a thermocouple should be annealed by passing a current through it at a white heat, when future changes will be slight if used in an oxidizing atmosphere. This annealing also will restore to very nearly its normal value the E.M.F. of couples which have been in contact with silicates.

Changes in temperature distribution along the wire may also affect the apparent electromotive force of the couple, causing apparent changes in temperature as great as 20° at 1000° C. with some wires. The less homogeneous the wires the more marked is this effect. In the most exact work, therefore, the same conditions of immersion must be followed throughout, or the resulting changes in E.M.F. measured.

It follows from all this, as Holborn and Day state, that the temperature scale, once established by means of the thermocouple, can be maintained with certainty only with the help of fixed temperatures such as the melting points. Dr. W. P. White draws particular attention to the importance of that region of the wires passing through a steep temperature gradient and the great influence that inhomogeneity in this portion of the wire may have upon the temperature readings with thermocouples.

If we consider an inhomogeneous thermocouple composed of short segments each of which is supposed homogeneous, at any junction of two segments there is developed an E.M.F. proportional to the temperature t and their difference in thermoelectric power ΔH, or for the whole circuit:

$$E = (t_1 \cdot \Delta H_1 + t_2 \cdot \Delta H_2 + \ . \ . \ . \ t_n \cdot \Delta H_n) = \Sigma t \cdot \Delta H.$$

It is evident that those portions of the circuit at constant temperature and of homogeneous material ($\Delta H = 0$) do not contribute to the value of E; but in the regions of temperature gradient of an inhomogeneous wire, the errors due to inhomogeneity depend also upon the temperature distribution along the wire. If an inhomogeneous thermocouple, therefore, is raised or lowered in a furnace at constant temperature, the reading of the couple will change. In view of these facts, it is important that those portions of the thermocouple wires passing from cold to hot regions be chemically and physically of uniform properties.

The effect of initial chemical inhomogeneity, for the platinum thermocouples, appears to be either negligible or very small, but may be considerable for base-metal couples. The region between hard-drawn and annealed wire is one of marked physical inhomogeneity. This can be, and should always be, eliminated by annealing the wires of most couples including platinum, preferably with an electric current, or by hardening in the case of constantan. The most troublesome source of inhomogeneity, however, the most difficult to remove, and the source of greatest error, particularly with platinum thermocouples, is that due to contamination from evaporation and diffusion of metal vapors into the region of temperature gradient of the platinum wire. The oxide coating which forms on some metals is also a similar source of uncertainty in the regions of variable temperature.

Regarding the effects of contamination of platinum wires, carbon, illuminating gas, and other reducing agents appear to act only through their reducing action on other substances, such as iron and silicon, capable of injuring the platinum. In an oxidizing atmosphere, iron oxides and silicates produce little or no effect; but metals such as iridium and rhodium, particularly the former, which is very volatile even from a Pt · Ir alloy wire at 900° C., and capable of alloying with platinum, will, if present, produce marked contamination of platinum wires. Amputation of the contaminated portions appears to be the only remedy in this case. Excessive local heating will also cause inhomogeneity to develop, especially in the alloy wire, probably due in part to evaporation and in part to crystallization.

Measurement of Inhomogeneity. — This is very easily and exactly effected, and should be carried out on any thermocouples to be used in work of high accuracy. Each of the wires is tested separately, its ends being kept conveniently at a constant temperature of 0°. The wire is in circuit with a sensitive galvanometer graduated in microvolts and is passed through a short electric resistance furnace kept at a constant temperature, 1000° or 1400° C. The readings of the galvanometer are taken for different positions of the furnace along the wire. The furnace may be replaced conveniently by a short length of porcelain heated by a Bunsen burner. Using a sensitive recorder, a small furnace may be pulled automatically along the wire which records its own variations. Such a device is in use at the Bureau of

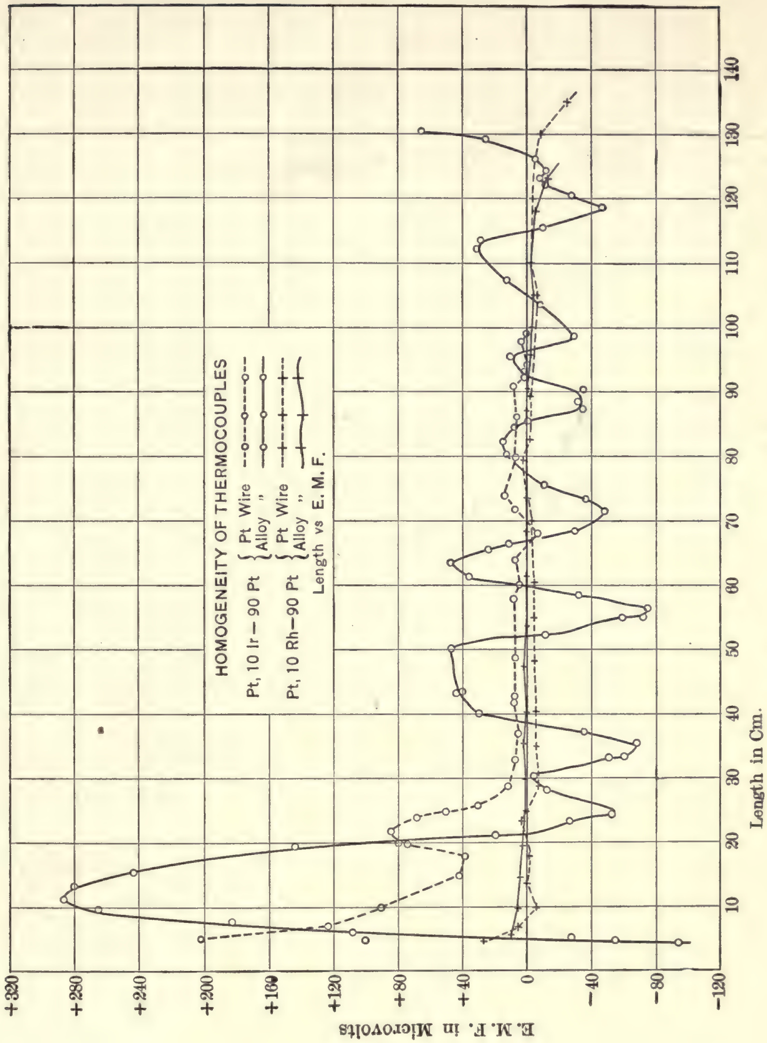


Fig. 46. Homogeneity of Thermocouples.

Standards. Another method is that shown in Fig. 47, which permits a point-to-point study of the phenomenon. In Fig. 46 are shown the homogeneity curves, taken by the first method, of the wires of two thermocouples, the one (Pt-Rh) new and of fresh, pure materials, the other (Pt-Ir) old and impure. These methods are easily sensitive enough to differentiate the various grades of platinum wire used in thermocouple manufacture.

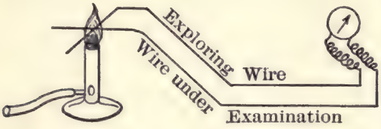


Fig. 47. Testing of Homogeneity.

We have already called attention to the inhomogeneity of base-metal thermocouples. We shall return to this question in a later paragraph.

Reproducibility of Thermoelectric Apparatus. — It is often of considerable convenience in all kinds of measurements, especially on a large scale with numerous working units of the same kind, to be able to duplicate or replace corresponding parts without having resort to new calibrations. This is equally desirable in temperature measurements, and in recent years there has been a large measure of success in the attempt to produce thermocouples and manufacture pyrometer galvanometers which are interchangeable.

As an example of the former, we may cite the case of the well-known 10 per cent platinum-rhodium normal thermocouples of Heræus. They are reported to have maintained the following constancy for the past six years:

AVERAGE E.M.F. AT 1000° C.

Year.	Millivolts.
1904	9.52
1905	9.53
1906	9.53
1907	9.57
1908	9.59
1909	9.55

Regarding the interchangeability of pyrometer galvanometers, the art of electrical instrument manufacture has so advanced in recent years that equivalent instruments, in error absolutely and with respect to each other by less than 10° C. throughout their scales, are produced currently by several makers.

Base-metal Thermocouples. — There appears to be an insistent demand, on the part of many in charge of technical processes requiring temperature control, for inexpensive and robust measuring apparatus. For this reason, if for no other, the use of the base-metal thermocouple has become firmly established. Its success has been due to several causes, principal among them being the production of fairly satisfactory alloys of high E.M.F. with temperature change, which can be made into practically unbreakable pyrometric canes of very low resistance; and the simultaneous development of pivot millivoltmeters suitable for use as galvanometers with this type of couple.

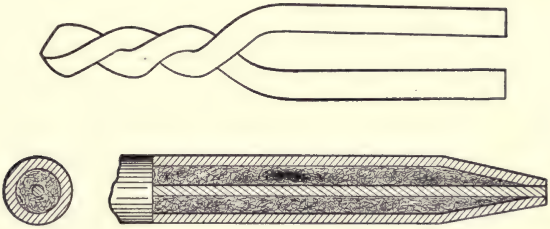


Fig. 48. Heavy Base-metal Welds.

Such canes can be had, for example, with a resistance as low as 0.05 ohms cold, increasing by only 0.01 ohm when heated to 1000° C. Even with a commercial millivoltmeter of only 1 ohm resistance, the calibration will remain constant, under these conditions, to 10° C. for any depth of immersion of the couple (see page 120). It is indispensable in such cases that *all* junctions be of negligible resistance, and they are preferably soldered. In Fig. 48 are illustrated two types of weld for base-metal couples.

A very considerable error, however, in the estimate of the temperature of regions into which are thrust thermocouples of considerable cross section and insufficient length, may arise from heat conduction along the pyrometer, the effect being to chill the hot junction below the temperature of its surroundings. It is important that such pyrometers be calibrated to allow for this effect.

The thermoelectric power of many of these base-metal couples is over 20 microvolts per 1° C., and some of them are 40 or more as compared with 10 microvolts per 1° C. for the ordinary platinum-rhodium couple. The low-resistance pivot galvanometers of 20 or 40 millivolts range, suitable for use with the base-metal couples, may be made more cheaply and robust than instruments suitable for use with platinum couples for the same sensibility.

As the base-metal couples receive hard usage, are cheap, and often require frequent replacing, it is of great advantage to make use of material of uniform thermoelectric properties, so that burned-out " fire ends " may be readily replaced as required without retesting. It is of course safer, and necessary in many instances, to calibrate each new fire end, either by comparison with a standard, or, as may be done conveniently even in technical plants, by taking the reading in salt baths of known freezing points (see page 190). In the case of the use of alloys or metals possessing critical regions, accompanied by the absorption or liberation of heat, it should be emphasized that discordant results may be obtained on reheating, the actual E.M.F.-temperature relation depending upon the internal structure of the material of the couple, and this in turn upon the rate of heating or cooling through these critical regions. These effects are particularly marked in couples of considerable size, and are enhanced by varying the depth of immersion of the couple in the test bath or furnace. We shall mention later some specific instances of these effects.

Although a very considerable number of base-metal thermocouples have been put upon the market in recent years, there appears to be very little certain knowledge available as to the exact composition, thermoelectric properties, and behavior of most of them, some of which are quite complex alloys, as for example of Ni, Cr, Al, and Cu. It should perhaps be noted that our use with base-metal couples of the adjectives " constant," "reproducible," etc., is not to be taken in the same rigorous sense as for the platinum couples.

Nickel-copper. — Various combinations of these metals have been used and recommended for temperatures as high as 900° C. According to the investigations of M. Pécheux, the most satisfactory one seems to be that with the alloy constantan (known also as "advance"), 60 Cu−40 Ni, as one wire and pure Cu as the other. The E.M.F.-temperature curve for this thermocouple approximates a fairly flat parabola, but appears to require an equation of the third or fourth degree in t to express the results with some exactness to 900° C.; or this interval may be divided into three, each of which is represented, to a fraction of a degree, by a parabola of the form $E_{t_1}^{t_2} = a + bt + ct^2$. Between 0 and 250° C. the numerical equation is roughly $E_0^t = 40\,t + 0.03\,t^2$ in microvolts for the copper-constantan thermocouple. Those with a smaller percentage of nickel have less flat curves, lower thermoelectric powers, and guard their original calibration less well than does the copper-constantan couple.

The limiting case in this series, that of pure nickel against pure copper, is of some interest, as it gives a good illustration of the effects of molecular transformation on thermoelectric behavior. Nickel undergoes such transformation between about 230° and 390° C., which causes both its electrical resistance and thermoelectric power to depart from their normal trend in this region. These effects are shown in Fig. 49, the data on resistance being from some measurements made by Somerville, on nickel wire, and on thermoelectric power of the Ni-Cu couple from the observations of M. Pécheux.

When, for such a couple, or any thermocouple in which nickel or any substance possessing regions of molecular transformation, its rate of heating or cooling is varied, the E.M.F. readings of the couple will not in general be the same for a given temperature within this region; and for rapid cooling, in some cases, especially for wires or rods of considerable diameter, the E.M.F.-temperature relations may be changed at all temperatures below this region as well, due to the retardation or partial prevention of the complete transformation by chilling. Reannealing and slow cooling will oftentimes restore the original annealed condition. The importance of annealing all such couples before their first calibration becomes apparent from the above considerations.

The presence of impurities appears to be a further source of considerable uncertainty in the constancy of these couples with continued use, it being noted, by Pécheux for example, that couples with very pure nickel remained more constant in use than those with the less pure metal.

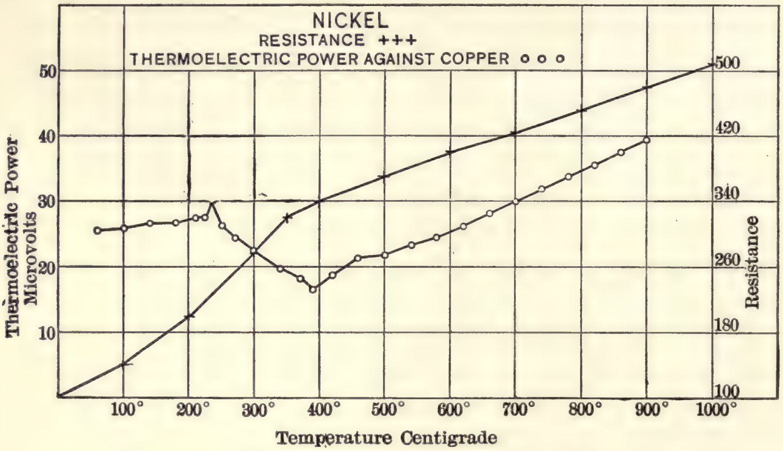


Fig. 49. Resistance and Thermoelectricity of Nickel.

The addition of zinc in any proportions to the copper-nickel alloy, giving the German silvers, appears to be detrimental in all respects.

The upper limit of 900°, assigned by Pécheux for the copper-constantan couples, is better replaced by 600°, or even less, for continued use with any considerable precision; and even at 600° both wires will oxidize and soon become fragile.

Nickel-iron. — We have already called attention to the behavior of iron wires and the enormous parasite E.M.F.'s that they may develop. Nevertheless, a favorite industrial thermoelectric combination has been, and still is in some quarters, a tube of soft iron inclosing a nickel wire. Nickel, associated with any other metal or alloy, will furnish a couple possessing anomalies in $\frac{dE}{dt}$ below 400° C., due to its molecular transformation region. Similarly, iron and also the various carbon- and alloy-steel wires have been found to introduce erratic thermoelectric behavior when used as one element in thermocouples.

Harrison, Barrett, Belloc, and others, who have studied in detail the behavior of such thermocouples, find, for example, that there are considerable changes in E.M.F.'s due to oxidation, carburization, reheating, rate of cooling, the nature of the furnace atmosphere, maximum temperature reached, and time of heating at any temperature; and in general, within any region of molecular transformation, the E.M.F. on cooling will differ from that on heating, producing E.M.F.-temperature cycles or hysteresis. The couples containing iron are most unreliable above 800° C., and all such couples, as well as those with wires of steel, nickel, copper, and many of their alloys, become brittle above 700° C.

The effect of reheating in producing hysteresis is shown in an experiment of Barrett on the change in temperature of the neutral point of a copper-steel couple:

NEUTRAL POINT OF COPPER-STEEL.

	Heating.		
	First.	Second.	Third.
When heating	328	283	268
When cooling	258	241	241

The E.M.F. is not always higher during heating, however, the following alloy for example giving lower E.M.F.'s against Cu, Pt, or Fe on heating. This alloy (Fe = 68.8, Ni = 25.0, Mn = 5.0, C = 1.2), due to Sir Robert Hadfield, also possesses the remarkable property of giving against a nearly pure iron an E.M.F. constant to within 4 per cent from 300° to 1050° C.

The variation in electromotive force with composition of steels against platinum has been studied by Belloc, whose results are shown in a somewhat idealized form in Fig. 23, page 110, from which it is evident that any changes in composition due to heating or atmosphere will produce great changes in the E.M.F. of such couples below 350° C. and above 700° C. By heating a platinum, 1.2 per cent carbon-steel couple fifteen times to 1000°, its E.M.F. per degree at 800° changed from 11 to 19 microvolts.

On the other hand, for relatively low temperatures, very exact measurements have been made with thermocouples made of iron or nickel and a base-metal alloy. Thus Palmer, working in the range 0° to 200° C. with an iron-constantan couple, gets a precision of 0.04 per cent when the residual E.M.F.'s, including those due to mechanical strains, are eliminated.

Complex Alloy Couples. — Several manufacturers have sought to produce base-metal couples which are free from some of the defects usually present in this type. The work done so far gives promise that this field of investigation is worthy of further development. Most of the effort has been on the modification of the iron and nickel elements by the addition of other metallic components such as tungsten, copper, chromium, cobalt, silicon, and aluminium. We may mention the Bristol, Thwing, and Hoskins couples as examples. One of the last, a robust nickel-chromium combination (Ni, 90 Ni − 10 Cr), has an E.M.F. about four times that of the ordinary Pt−Rh couples, the E.M.F.-temperature relation is nearly linear to 1400° C. without any recalescence disturbances of sufficient magnitude to seriously affect the temperature readings in technical work, and after annealing this couple retains its readings sufficiently for many commercial uses, even when heated to over 1300° C. for short periods.

For high temperatures, the Hoskins Company now use principally the couple nickel aluminium (2% Al) − nickel chromium (10% Cr); and for low temperatures, nickel copper (65% Cu) − nickel chromium (10% Cr). The characteristics of the materials used in the Hoskins couples are given by M. A. L. Marsh, as shown in the accompanying table:

HOSKINS' THERMOCOUPLE CALIBRATIONS. COLD JUNCTION AT 25° C.

Couple.		Millivolts.					
Positive element.	Negative element.	100° C.	232° C.	419° C.	657° C.	800° C.	1065° C.
Nickel	Nickel chromium, 10% Cr.	3.21	9.34	16.88	26.0	31.50	41.80
Nickel aluminium, 2% Al	Nickel chromium, 10% Cr.	....	9.35	17.60	28.10	34.53	46.20
Nickel aluminium, 3⅓% Al	Nickel chromium, 10% Cr.	....	8.75	17.20	28.25	35.00	47.20
Nickel aluminium, 5% Al	Nickel chromium, 10% Cr.	....	8.25	16.67	.....	.....	47.00
Cobalt	Nickel chromium, 10% Cr.	3.09	9.93	20.96	33.18	.....	45.58
Nickel copper, 65% Cu	Nickel chromium, 10% Cr.	4.39	13.15	27.27	44.66	.....	75.40
Copper	Nickel chromium, 10% Cr.	1.48	4.15	7.73	11.27	.....	13.57

ELECTRICAL RESISTANCE OF THERMOCOUPLE ELEMENTS.

Element.	Resistance per foot, 0.40 m/m. wire, at 25° C.	Specific resistance at 25° C.	Temperature coefficient per degree C.
Nickel	0.26 ohm	10.34	0.00415
Nickel aluminium, 3⅓% Al	.63	25.0	.00274
Cobalt	.356	14.15	......
Nickel copper, 65% Cu	.99	39.3	......
Copper	.043	1.75	.00388
Nickel chromium, 10% Cr	1.76	70.0	.00051

A difficulty met with in the manufacture of complex alloy couples is the reproducibility of the same E.M.F.-temperature relation from one casting to another. The identity of behavior is, however, highly desirable in cheap commercial couples which are frequently replaced, as it obviates the necessity of recalibration or adjustment of the galvanometer scale for each couple.

The Noble Metals: Geibel's Data. — We have already discussed the thermoelectric behavior of the platinum-rhodium alloys, page 116. Some of the platinum group metals and alloys have been studied by Holborn and Day, Rudolphi, Doerinckel, and others. The most thorough and reliable investigation, however, of the electrical and mechanical properties of the noble metals and their alloys, in view of their availability for temperature measurement, has been made by W. Geibel in the laboratory of the Heræus platinum works, using materials much purer than could be obtained by Barus or Le Chatelier twenty-five years ago. The data of Geibel show wide differences from the earlier results of these observers.

PROPERTIES OF THE NOBLE

Metal or alloy.	Electromotive force (millivolts) against								
	100°	200°	300°	400°	500°	600°	700°	800°	900°
Pd I	......	......	− 1.1	− 1.6	− 2.4	− 3.3	− 4.5	− 5.8	− 7.3
Pd II	......	− 1.1	− 1.8	− 2.6	− 3.4	− 4.6	− 6.0	− 7.5	− 9.2
Pd−Au 10	......	− 1.9	− 2.9	− 4.1	− 5.4	− 6.9	− 8.4	−10.2	−12.1
Pd−Au 40	......	− 4.1	− 6.4	− 9.4	−12.5	−16.0	−19.7	−23.4	−27.3
Pd−Au 60	−3.8	− 7.0	−10.5	−15.0	−19.7	−24.2	−28.8	−33.5	−38.2
Pd−Au 80	−0.5	− 1.0	− 1.7	− 2.5	− 3.4	− 4.4	− 5.5	− 6.8	− 8.2
Au	+0.8	+ 1.8	+ 3.1	+ 4.5	+ 6.2	+ 8.0	+ 9.9	+12.0	+14.2
Pd−Ag 10	−0.9	− 2.0	− 3.3	− 5.0	− 6.8	− 9.0	−11.4	−14.2	−17.0
Pd−Ag 20	−1.8	− 3.5	− 5.7	− 8.5	−11.7	−15.2	−19.2	−23.2	−27.4
Pd−Ag 40	−3.7	− 6.8	−10.7	−15.3	−20.2	−25.4	−31.0	−36.5	−42.1
Pd−Ag 80	−0.1	− 0.2	......	− 0.3	......	− 0.4	......	− 0.5	− 0.6
Ag	+0.7	+ 1.7	+ 2.9	+ 4.4	+ 6.1	+ 8.2	+10.6	+13.1	+15.9
Pd−Pt 10	+0.3	+ 0.6	+ 0.8	+ 1.0	+ 1.0	+ 0.8	+ 0.6	+ 0.1	− 0.6
Pd−Pt 30	+0.8	+ 1.6	+ 2.5	+ 3.5	+ 4.4	+ 5.3	+ 6.2	+ 6.8	+ 7.4
Pd−Pt 60	+0.7	+ 1.5	+ 2.3	+ 3.3	+ 4.4	+ 5.4	+ 6.5	+ 7.6	+ 8.5
Pd−Pt 90	+0.3	+ 0.7	+ 1.2	+ 1.7	+ 2.3	+ 2.7	+ 3.2	+ 3.7	+ 4.2
Pt	......	......	......	......	......	......	......	......	......
Pt−Ir 5	+1.1	+ 2.1	+ 3.2	+ 4.3	+ 5.4	+ 6.5	+ 7.6	+ 8.7	+ 9.7
Pt−Ir 10	+1.3	+ 2.6	+ 4.1	+ 5.8	+ 7.4	+ 9.1	+10.7	+12.3	+14.0
Pt−Ir 25	+1.2	+ 2.6	+ 4.3	+ 6.2	+ 8.2	+10.4	+12.6	+14.8	+17.1
Pt−Ir 35	+1.1	+ 2.5	+ 4.1	+ 5.9	+ 7.9	+ 9.9	+12.1	+14.4	+16.8
Ir*	+0.65	+ 1.5	+ 2.5	+ 3.6	+ 4.8	+ 6.1	+ 7.6	+ 9.1	+10.3
Rh*	+0.65	+ 1.5	+ 2.6	+ 3.7	+ 5.1	+ 6.5	+ 8.1	+ 9.9	+11.7
Au−Pt 10 Au−Pt 20 Au−Pt 40	Not constant, variations as great as 2 millivolts at								
Ag−Pt 10	+0.2	+ 0.4	+ 0.7	1.3 1.0	1.8 1.5	2.4 2.1	3.1 2.8	3.8 3.6	4.7 4.5
Ag−Pt 30	−0.4	− 0.8	− 1.4	2.0 2.1	2.6 2.8	3.5 3.7	4.5 4.7	5.5 5.7	6.6 6.8

* Holborn and Day.

Some of his results, taken from a very complete series, on E.M.F. against platinum, electrical conductivity, temperature coefficient, and tensile strength, are given in the accompanying table. Wires of 1.3 mm. were first glowed and then cold-drawn to 1 mm. Compositions are per cent by weight. The tensile strength may be taken as giving an approximate measure of hardness.

One of the most satisfactory combinations for use as thermo-couple to say 1000° C. appears to be 40 Pd · 60 Au − Pt, which at 1000° C. gives four times the E.M.F. of the ordinary Le Chatelier couple. This Pd · Au alloy also has a very low temperature

METALS AND THEIR ALLOYS. (GEIBEL.)

platinum.			Electrical conductivity × 10⁻⁴ at 0° C.	Temperature coefficient between 0° and 160°.	Tensile strength in kg. for 1 mm. wire.	Melting begins. From various observers.
1000°	1100°	1200°				
− 8.9			9.47	0.00328	30	1550
−11.0	−13.0	−15.0				
−14.0			7.01	.00224	36	1545
−30.9			3.96	.00079	43	1500
−42.7			4.05	.00034	49	1450
− 9.8			7.94	.00064	45	1350
+16.5			47.52	.00326	21.5	1063
			4.85	.00117	42	1500
			3.26	.00066	49.5	1450
			2.38	.00005	51	1350
			9.58	.00047	40	1110
			63.72	.0041	31	960
− 1.5	− 2.5	− 3.7	6.93	.00214	33	1570?
+ 7.9	+ 8.1	+ 8.2	4.57	.00128	(39)	
+ 9.5	+10.6	+11.5	3.78	.00096	(43)	
+ 4.7	+ 5.2	+ 5.7	5.38	.00136	42	1730?
			9.94	.00348	24	1755
+10.7	+11.8		5.61	.00188	40	1780?
+15.7	+17.3	+19.0	4.34	.00126	48	
+19.4	+21.8	+24.3	3.17	.00066	98	
+19.1	+21.6	+24.3	2.71	.00058	126	
+12.6	+14.5					2300
+13.7	+15.8					1920
high temperatures.			9.76	.00098	32	1630
			5.57	.00054	52	1510
			3.06	.00037	69	1340
Before heating						1450?
After heating						
Before heating						1200?
After heating						

coefficient and resembles the 10 per cent iridium alloy of platinum in hardness.

The alloys of platinum with gold or silver are evidently unsuitable for use in thermocouples, due to great changes in E.M.F. with prolonged heating. Geibel gives also data showing the effect of annealing at various temperatures upon tensile strength for some of these alloys. The effect is most marked for those alloys which show corresponding changes in E.M.F. For the Pt-Ir alloys there is little effect of annealing until 600° is reached, but after annealing above 800° the tensile strength (cold) falls off rapidly with increase in temperature. For pure platinum this decreases regularly from 32 kg. for the hard-drawn to 17 kg. after annealing at 1300° C.

The alloy 60 Pd · 40 Ag has nearly a zero temperature coefficient. If of sufficient permanence in its properties, when joined to 90 Pt · 10 Ir, for example, we should have a couple of nearly constant resistance seven times as sensitive as 90 Pt · 10 Rh − Pt at 900° C.

All the alloys noted in the table appear to be solid solutions with no transformation or critical points.

Special Couples. — We may mention certain couples that can be classed neither as base-metal nor as platinum thermocouples, some suitable for relatively low temperatures and others for the very highest.

Silver-constantan is a combination that is used considerably and appears to give satisfaction to temperatures as high as 700° C.

Silver-nickel has also been used by Hevesy and Wolff from −80° to 920° C. The thermoelectric power is about three times that of the Pt-Rh couple, but is quite variable, and there is no simple formula expressing the E.M.F.-temperature relation even above 400° C.

Iridium-ruthenium. — The upper limit for the continued use without frequent recalibration of the platinum-rhodium couple is about 1600° C., although the melting point of platinum may be reached with it. Heræus has met the need for a couple that can be used to very much higher temperatures by constructing one having for one lead pure iridium and for the other an alloy of 90 parts iridium to 10 parts ruthenium, with which temperatures to about 2100° C. may be measured. The E.M.F.-temperature relation for these couples is not quite linear.

Calibrations may be made in a suitable furnace by comparison with a Pt-Rh couple or by taking readings at the melting points of Au, Pd, and Pt, above which temperature extrapolation must be resorted to unless pure Rh is available as a calibration point, or comparison be made with an optical pyrometer.

The indications of this couple remain fairly constant with repeated heatings considering the extremely high temperatures to which it may be exposed. Inhomogeneity will of course develop. A serious source of error, noninherent in this couple alone, is that due to heat conduction along the thick leads, which may amount to 50 degrees at the higher temperatures unless allowed for by observing some known temperature, as the Pt point, with the same immersion as used in the experiments.

This thermocouple, on account of its very great fragility when cold, is not suited for any ordinary industrial uses, and must be handled with the greatest care; it is also, of course, very expensive.

Compound Thermocouples. — These are of two kinds, the object of the first being to give greater sensibility to the couple by increasing its E.M.F. This is usually accomplished by putting two or more thermocouples in series, when the available E.M.F. is increased in the proportion to the number of couples. It should be remembered, however, that, by this operation, the electrical resistance of the circuit is also proportionally increased, and this may introduce considerable errors when indicating galvanometers of relatively low resistance are used; and in this case also, the sensibility may not be increased enough to warrant the additional couples, which are, of course, expensive if the platinum metals are used. The effects of varying depths of immersion of the couple wires in the heated space and changes of zero are also accentuated by this method, which, with the recent development of galvanometers which are both sensitive and robust, becomes superfluous in ordinary cases. For measuring small temperature differences, however, as in detecting transformation points, this method has its advantages.

The other kind of compound thermoelectric couple, which in the following form appears to be due to Bristol, was designed for the elimination of a portion of the expensive platinum and platinum-rhodium wires. It consists in the substitution of inexpensive alloys for the part of the couple which is not exposed to a temperature above a red heat, as shown in Fig. 50, these alloys being so chosen as to give the same E.M.F.-temperature relation as the platinum-rhodium couple; so that the resultant E.M.F. generated by the compound couple is the same as if the entire couple were of platinum and platinum-rhodium.

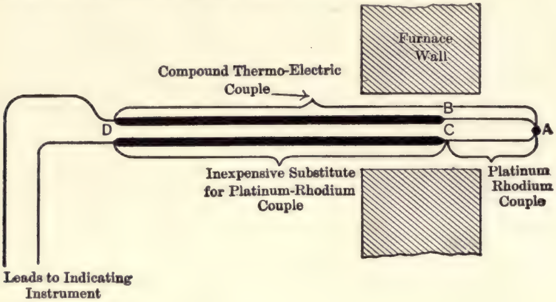

Furnace Wall
Compound Thermo-Electric Couple
B
D
C
A
Inexpensive Substitute for Platinum-Rhodium Couple
Platinum Rhodium Couple
Leads to Indicating Instrument

Fig. 50. Bristol's Compound Couple.

In England, Peake proposes to use, with platinum-iridium or rhodium couples, such compensating leads, made with one wire of copper and the other of cupronickel (Ni from 0.1 to 5 per cent). That good compensation may be obtained by this method is shown by the following table from products used by the Cambridge Scientific Instrument Company:

PEAKE'S COMPENSATING LEADS.

Temperature.	Pt – Pt · Ir couple.	Compensating leads.
° C.	Millivolts.	Millivolts.
0	0	0
50	0.59	0.60
100	1.25	1.25
150	1.95	1.90
200	2.68	2.60
250	3.42	3.40
300	4.20	4.25

The compensating couple of Chauvin and Arnoux is the result of an attempt to eliminate the considerable length of wire and relatively high resistance of the platinum thermocouple, and at the same time keep the advantages of such a couple for industrial measurements to 1600° C. with a pivot instrument of robust type in those cases where it is not necessary to have a considerable length of wire exposed to the hottest temperatures. The arrangement shown in Fig. 51 consists in measuring the temperature in two steps. The platinum-iridium couple is in series with one of iron-constantan, whose hot junction is placed beside the cold junction of the platinum couple. On account of the greater E.M.F. of the iron-constantan couple, it is necessary to shunt this last with a resistance to give the same temperature difference. This shunt reduces the total resistance and so facilitates the use of long canes.

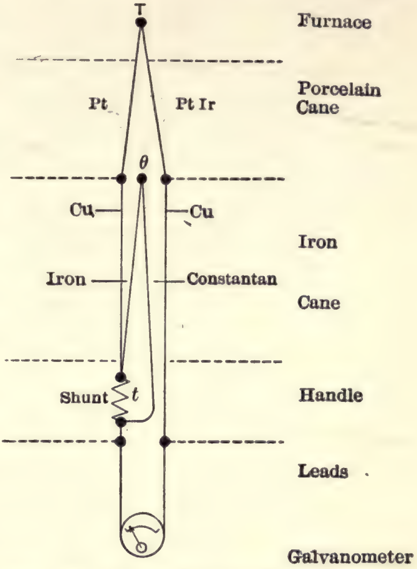


Fig. 51. Compound Couple of Chauvin and Arnoux.

Referring to the figure, we have for the platinum-iridium couple:

$$e = f(T - \theta),$$

and for the iron-constantan couple:

$$e_1 = f'(\theta - t).$$

Now, if the alloys are properly chosen in composition, it appears to be possible to so adjust the shunt as to obtain E.M.F.-temperature curves superposable for the two couples between θ and t, which is equivalent to having a single platinum-iridium couple, whence:

$$E = e + e_1 = f(T - t).$$

The value of the shunt resistance can be shown to depend only on the resistance of the compensating couple and on the ratio of the two thermoelectric powers.

The temperature θ should not exceed 800° C., and a very pure iron tube should be used to prevent anomalies around 700° C.

Calibration of Thermocouples. — With the several national standardizing laboratories organized and equipped for such work as the calibration of pyrometers, it is no longer necessary for an individual to concern himself with this matter. Nevertheless, it is often desirable to be able to carry out such calibrations simultaneously with other investigations or with the apparatus in hand. We shall not concern ourselves with descriptions of the calibration of the electrical measuring apparatus used, such as millivoltmeters and potentiometers; they will be found in any book on the testing of electrical apparatus. It is rare that an individual is so situated as to have the equipment necessary for these electrical calibrations, when recourse must be had to the standardizing laboratories. In the case of thermocouples, however, used with pyrometer galvanometers possessing a millivolt scale which is approximately correct or a scale of equal parts, the calibration of the thermocouple and galvanometer may be effected simultaneously to a relatively high degree of accuracy by taking a sufficient number of fixed points with the couple joined to its galvanometer.

We shall assume, therefore, either that the measuring apparatus is correct or that it may be sufficiently well calibrated by the operations carried out on the thermocouple.

We shall consider first the requirements for the highest accuracy attainable with platinum-metal thermocouples suitable for high temperatures, and then methods applicable to industrial practice and for base-metal couples.

Precision Calibration. — We have seen that for an accuracy of better than 5 degrees, or in many cases of 10 degrees, it is necessary to use the potentiometric method of measurement. The cold junctions of the couple should be kept at 0° C., and the wires of the couple should be annealed and shown to be sufficiently homogeneous. Only couples of the platinum metals should be used, at least for temperatures above 600° C.

The calibration may be carried out by the use of melting and boiling points of known values, or by comparison in a suitable furnace with one or more standardized pyrometers. Great care has to be taken with the insulation of the thermocouple circuit, especially at high temperatures and when electric heating is used. Reversal of the heating circuit will show this effect. It is also necessary to insure sufficient depth of immersion in the bath or furnace to avoid errors due to heat conduction along the wires of the couple. This can be tested by changing the depth of immersion in the region of constant temperature, when the readings should not change, provided of course the wires are homogeneous.

Crucible Method. — In the case of the metals or salts which are used to give the temperature of their freezing or melting points, it is usually better in exact work to use crucibles containing a considerable quantity of the material, 300 c.c. or more, although a skilled observer using a suitable furnace can get good results with very small quantities of material. Either gas or electric furnaces may be used. The latter permit a more delicate control both of the rate of cooling and of the atmosphere in which the melting or freezing is carried out, but the former can usually be heated much more rapidly. For work to 1° it is better to keep to the electric furnace.

As to the choice between melting and freezing points, the consensus of opinion is in favor of the latter when possible as being usually sharper, although sometimes complicated by undercooling, as in the case of the metals antimony and tin. With some salts this phenomenon is prohibitive of using the freezing point.

The crucibles should of course be of material that does not react with the charge or the atmosphere of the furnace, dissolve in the former, or let the furnace atmosphere penetrate into the charge when they react with each other. For salts, the best material for the crucible is platinum, but nickel crucibles will also answer in many cases, and they are inexpensive. Fire-clay crucibles, and even those of porcelain, may be used with certain salts. For the nonoxidizable metals there are several substances available, such as porcelain, magnesia, lime, alumina, graphite, and quartz. The oxidizable metals which do not dissolve graphite are best melted in graphite crucibles, those of the Acheson Company being almost pure graphite. A crucible only partly of graphite, such as the Dixon crucibles, is often sufficient, and lasts longer than those of pure graphite, and is to be preferred when a gas furnace is used. These crucibles should have covers, and in addition the surface of the metal should be covered with powdered graphite. In some cases a gas, such as CO or H, which acts as a reducing agent, or prevents oxidation such as N, must be led into the furnace. With the gas furnace, it is well to prevent the direct play of the flames on the crucible by surrounding the latter with a cylinder of metal such as wrought iron, which helps equalize temperature within the crucible.

There are a considerable number of makers of crucible furnaces, both gas and electric, suitable for ordinary freezing-point determinations. For the attainment of the higher temperatures with the former an air blast is necessary, and for the latter a rheostat and ammeter or voltmeter are necessary auxiliaries.

The electric method of heating was first used in pyrometric work for the determination of fixed points by means of the thermocouple by D. Berthelot in France and Holborn and Day in Germany. The earlier furnaces were constructed by winding pure nickel or platinum wire on porcelain tubes inclosed in an outer tube of porcelain and wrapped in asbestos. The nickel-wound furnaces may be used up to 1300° C. for a short time with care and they are readily rewound when burnt out. Their life is prolonged by packing the wire so as to prevent access of air. The platinum-wire furnaces are very expensive, but may be used up to 1500° C. These last have since been pretty generally displaced by furnaces of the Heræus type, which are made by winding platinum *foil* of about 0.007 mm. thickness on porcelain tubes covered with an aluminium earth paste which does not attack platinum at high temperatures. These furnaces are inexpensive and very durable to 1300° when carefully used. Heræus also manufactures iridium resistance furnaces with which temperatures over 2000° C. may be reached, and a very constant temperature maintained. With this type, special precautions have to be taken to prevent the evaporation of iridium on to thermocouple wires. A further advantage, in some cases, of the electric furnace is the absence of reducing gases.

The use of electric heating has rendered the standardization of the thermocouple and all other pyrometers a relatively easy matter and increased greatly the accuracy and range attainable in establishing the fixed points in pyrometry.

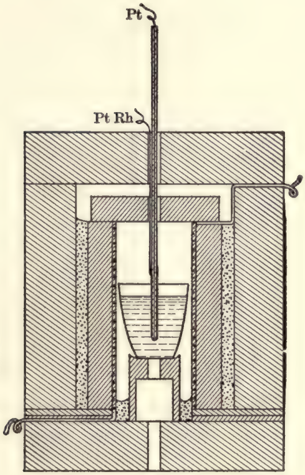


Fig. 52. Electrical Crucible Furnace.

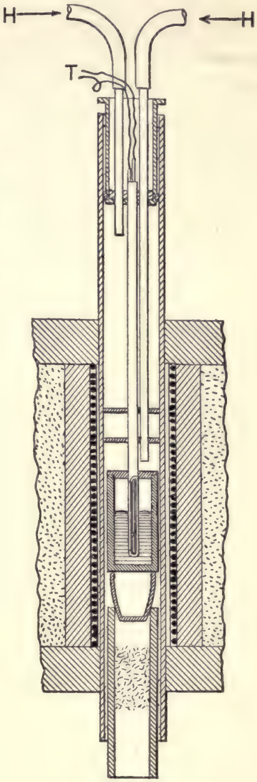


Fig. 53. Electrical Crucible Furnace.

Types of electric crucible furnaces are shown in Figs. 52, 53, and 175. In those of the Geophysical Laboratory (52 and 53), the platinum heating coil is embedded in Marquardt mixture.

Among the gas crucible furnaces we may mention those of the

Buffalo and the White Dental companies, the American Gas Furnace Company, and the Méker furnaces. A form of furnace that Le Chatelier found very serviceable is shown in Fig. 54. It is a furnace of English design, which has the advantage to resist almost indefinitely the action of heat and to be very easily repaired. The principle of the construction of these furnaces is to make them of two concentric layers. The outer covering of fire clay, bound together by iron, gives solidity to the furnace; it receives but indirectly the action of the heat, and is not exposed to cracking by shrinkage under the action of too high temperatures. The inner envelope, which alone receives the action of the heat, is made of large-grained quartz sand, grains of 1 mm., mixed with a small amount of a flux. At a high temperature the quartz does not shrink as does clay; it expands, on the contrary, passing over to the form of amorphous silica with a change of density from 2.6 to 2.2. But this transformation is effected only with extreme slowness, otherwise it would burst the furnace. If by chance this inner lining falls down, it is easily replaced by putting into the furnace a glass jar of suitable diameter, surrounded with a sheet of oiled paper, and packing about this coarse quartz sand slightly moistened with a sirupy solution of alkaline silicate. The furnace is heated by means of a lateral opening with a Fletcher lamp, which has the advantage of being sturdy, or with an ordinary blast lamp.

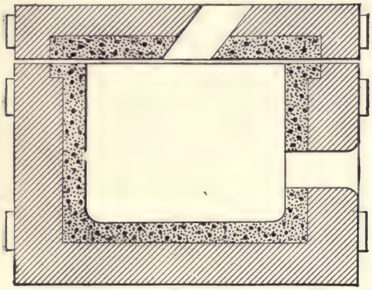


Fig. 54. Gas Crucible Furnace.

Among the metals which can be used, or which are not too expensive for the calibration of thermocouples by the crucible method, are Sn, Cd, Pb, Zn, Al, Sb, Ag, Cu, Ni, Fe, and Co. The last four are readily oxidizable, as is also Sb, but its oxide does not appear to dissolve in the metal; while Ag absorbs oxygen from the air unless protected. Al attacks crucibles containing silica, and is difficult of manipulation. The behavior of these metals is discussed at length in Chapter XI. If only three points are required, Zn, Sb, and Cu will suffice if the last two are manipulated in a strictly reducing atmosphere. It is, of course, absolutely essential that the purity of the metals used can be vouched for. The eutectic Cu-Cu_2O is well fixed, as is also the alloy Cu_2-Ag_3, to serve for thermo-couple calibrations.

The exact values of the freezing point of very few salts are well known, as is shown on page 190. NaCl is perhaps the most certainly determined and is conveniently located between Sb and Cu to serve as a fourth calibration point; other well-known salts are Na_2SO_4 and chemically prepared diopside ($CaSiO_3 \cdot MgSiO_3$). A thin platinum detachable crucible used at the Geophysical Laboratory with small quantities of salt, into which the couple may be dipped, is shown in Fig. 55.

Some of the salts will attack the porcelain sheath about the thermocouple. A metal one, platinum or nickel, may be substituted, taking care to keep the wires of the thermocouple insulated. The metals act variously on the porcelain tubes. If left in zinc they will invariably break on cooling. If withdrawn from liquid aluminium, unless greatly overheated, they will likewise break if any metal adheres to the porcelain. The Al also dissolves silica. They may be left in copper, however, and reheated without cracking. The best practice is to always withdraw from the liquid the porcelain or other protecting tube without any substance sticking to it after finishing the observations with any metal or salt. The use of quartz-glass protecting tubes will in general prove disappointing.

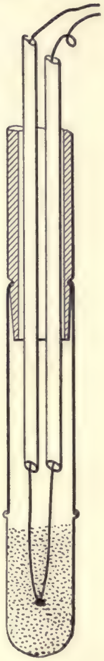


Fig. 55. Detachable Platinum Crucible.

Wire Method. — Measurements of the melting points of a precision of one or two degrees may be obtained with the nonoxidizable metals, which can be drawn, such as Au (1063°), Pd (1550°), and, to a slightly less precision, Pt (1755°), by inserting a short length of wire between the two wires of the hot junction of the thermocouple and gradually raising the temperature until the circuit breaks, due to the melting of the interposed link, and noting the maximum reading. Only a millimeter or two of the couple wire need be lost by this operation. The best results are obtained in a clear resistance-tube furnace of small diameter; the Pt point cannot be obtained in this way except in some special form of carbon furnace (Fig. 56), or in an iridium- or platinum-alloy furnace (see Fig. 174, Chap. XI). The wires should be protected by porcelain, quartz-glass, or magnesia tubes. In any case the link should be fused, not tied into place, and is best of nearly the same diameter as the couple wires. Very great precautions

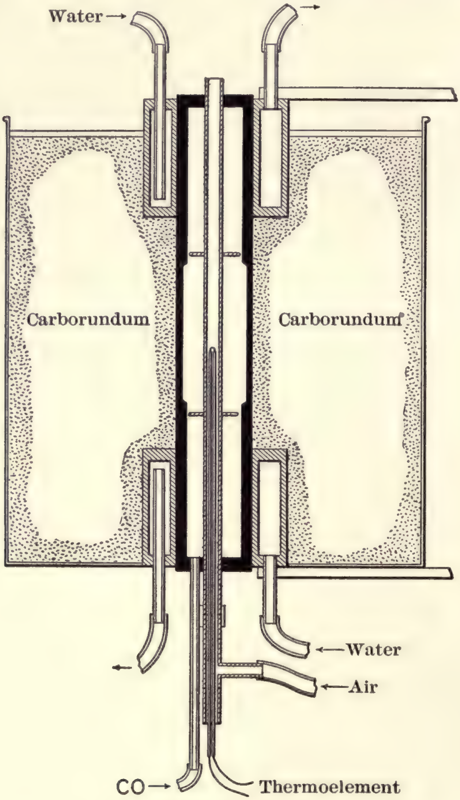


Fig. 56. Sosman's Carbon Furnace.

have to be taken to guard against leaks from the furnace, it being absolutely necessary that no part of the thermocouple circuit touch any hot part of the furnace in the case of Pd and Pt melts, and the insulators of the separate leads should not touch each other within the furnace.

In general, much less reliable results will be obtained when the oxyhydrogen or other flame has to be used. The unsteadiness of the flame may be partly overcome by immersing the linked or wrapped junction in a small muffle or in a small crucible containing powdered refractory material such as alumina. For the platinum point the oxyhydrogen flame is required; the palladium point can be obtained with a strong blast, and the gold point with an ordinary Bunsen. In industrial plants advantage may be taken of flues, furnaces, etc., to give the requisite heat.

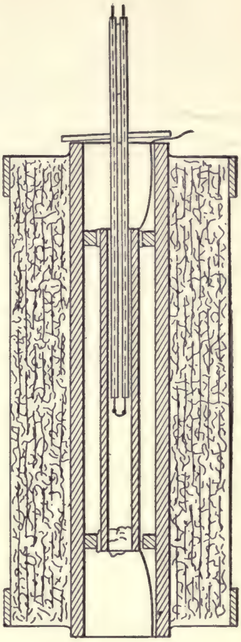


Fig. 57. Mounting for Wire Method.

The precision obtainable with the wire method is illustrated by observations of Waidner and Burgess on the melting point of palladium, carried out in an electric resistance furnace (Fig. 57), the palladium wire being inserted at the junctions of a series of Pt-Rh and Pt-Ir couples. The temperature scale of the Table, page 186, is that of the thermocouple (equation (3), page 112).

Instead of inserting the link in the thermocouple circuit, it may be put in a neighboring auxiliary circuit containing some electrical device for recognizing a break. The accuracy will be somewhat lessened, but the protected couple will remain intact by this modification.

A wire method devised by Wright suitable for use with minute quantities of salts is shown in Fig. 58. The salt is mounted at T on the slightly flattened junction within a water-jacketed electric furnace placed below a microscope, by means of which the melting or freezing is observed.

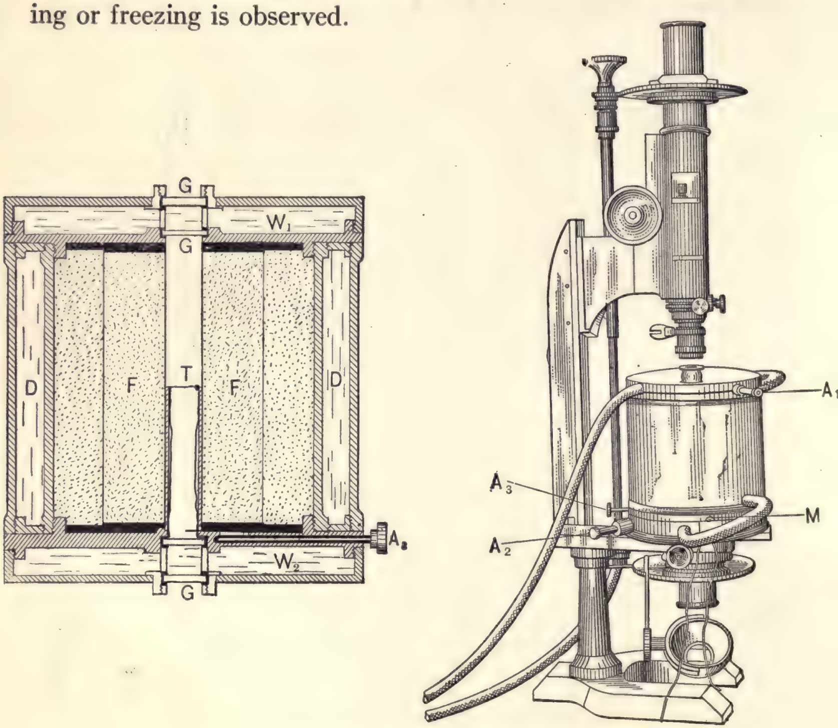


Fig. 58. Furnace and Microscope for Minute Pieces.

MELTING POINT OF PALLADIUM — WIRE METHOD.

Thermo-couple.	Number of observations.	Melting point of palladium.	Remarks.
W_1	5	1531.0°	Horizontal furnace; bare wires.
S_2	6	1530.5	Horizontal furnace; porcelain tubes.
W_3	4	1530.0	" "
P_2	5	1529.5	" "
P_1	2	1530.0	Vertical furnace; see Fig. 57.
S_2	2	1530.5	" "
P_2	2	1530.0	" "
W_1	3	1530.5	" "
W_6	6	1530.1	" "
	Mean =	1530.2°	M.P. on thermoelectric scale (equation (3), p. 112).

Boiling points, including those of the metals such as Cd and Zn, have frequently been used for the calibration of thermocouples, but the boiling metals are much more difficult to manipulate than the melting, and there is far greater danger of contamination of the thermocouples, nor is there need of resorting to them. If desired, however, the freezing points of Sn, Pb or Cd, and Zn may be replaced by the boiling points of naphthaline, benzophenone, and sulphur respectively, none of which attack the couples ordinarily used. The standard form of boiling apparatus for an accuracy of 0.05° C. or better is shown in Fig. 169, except that for naphthalene and benzophenone a side condenser tube should be added; or an air blast from a ring burner around the top of the boiling-tube may be used.

For a somewhat less accuracy the smaller portable apparatus of Barus (Fig. 59) may be used for boiling points, including also water and analine. This consists of a tube of thin glass, similar to test tubes, of 15 mm. inside diameter, 300 mm. long, with a small bulb at 50 mm. below the open end. It is surrounded with a plaster muff of 150 mm. height and 100 mm. diameter which has been cast about the glass tube inside of a thin metallic cylinder forming the outside surface. The bulb is immediately above the plaster jacket, below which the tube, closed at its lower end, extends to a distance of 70 mm. As soon as the plaster has begun to set the glass tube is taken out, giving it a slight twisting motion. The cylinder is left to dry, and the tube is again put in place. This allows, when the tube is broken, of taking it out and replacing it, which would be difficult if it adhered to the plaster. A jacketed Victor Meyer tube may also be used.

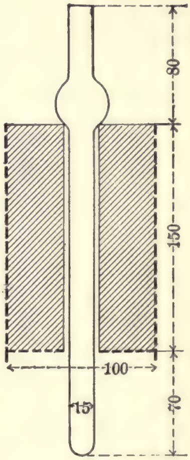


Fig. 59. Boiling Apparatus of Barus.

The lower free portion is heated by a Bunsen flame gently at first, then without any special precaution, once boiling sets in. The liquid at rest should occupy two-thirds of the height of the free end of the tube. The heating is continued until the liquid coming from the condensation of the vapor runs abundantly down the walls of the bulb. The flame is then adjusted so that the limit of condensation of the liquid, which is very sharp, remains constantly midway up the bulb. There is then a very uniform temperature in the interior of the glass tube throughout the height of the plaster cylinder. The junction of the couple is inserted and the coil of the galvanometer takes up a fixed invariable position. It is well to prevent the liquid from running down about the couple by placing a small cone of aluminium or asbestos above the junction. Electric heating may also be used.

For the boiling point of zinc, Barus made small crucibles of porcelain very ingeniously arranged, but also very complicated, besides being fragile and costly. One can make use more simply of a porcelain crucible 70 mm. deep (Fig. 60), filled with melted zinc for 50 mm. of its depth, and, above, 20 mm. of charcoal dust. A cone pierced with a central hole lets pass a small porcelain tube containing the couple. The whole is heated until there is seen a small white flame of zinc escaping from the crucible. It is indispensable that the openings for the escape of zinc vapor be large enough. They tend, indeed, to become clogged by a deposit of zinc oxide which solders at the same time the cover to the crucible, and this causes an explosion when there is no longer vent for the zinc vapors. A better form providing for the condensation of vapors was used by D. Berthelot.

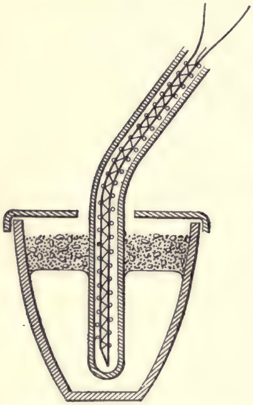


Fig. 60. Zinc-boiling Apparatus.

Technical Calibrations. — The process of calibration is greatly simplified if an uncertainty of 5° C. or more may be permitted, as is the case for most technical operations. When the crucible method is used, smaller crucibles and furnaces may be allowed than for exact calibration, and metals and salts of less certain purity may be tolerated, although it is most certainly safer to use only very pure materials. Some metals, such as Al and Sb, have their melting points greatly influenced by small impurities, and are obtainable in sufficient purity with difficulty. Other metals, such as Sn, Pb, Zn, and Cu, can be trusted from almost any source of supply to give temperatures to within 2° C. of the melting points of the pure metals. The precautions of manipulation mentioned in the preceding paragraphs apply here, with somewhat attenuated emphasis, depending upon the accuracy desired. For example, it is often not convenient to maintain the cold junctions at 0° C., or one may desire to keep them during calibration at the average temperature to which they are subjected in use or attached directly to the pyrometer galvanometer. We have indicated elsewhere (page 155) how to make allowance for variations in cold-junction temperatures.

The galvanometer and thermocouple may be tested either together or separately, but the former method is the more convenient and eliminates the use of any auxiliary apparatus. Five or six points on the galvanometer scale are usually sufficient for a technical calibration of the couple and galvanometer together. These may be given by any of the freezing or boiling points we have mentioned. A convenient inexpensive series of the former, requiring the minimum of precautions in manipulation and suitable in crucibles of 50 or 100 c.c. in a small air-gas furnace when the couples are wires of small diameter, is the following:

Sn	232° C.	Al	657° C.
Pb	327	NaCl	800
Zn	419	$Cu \cdot CuO_2$	1063

The last is copper saturated with its oxide. A piece of carbon steel (0.9 per cent C) bored with a small hole into which the couple is inserted will give on cooling a calibration temperature of about 700° C.

If it is desired to use salts only, as may be the case with certain base-metal couples of the cane type, which are plunged without protection directly into the bath, there will be some sacrifice of accuracy even when large quantities of salt are used in nickel crucibles, due in part to our uncertainty of their melting points, in part to the great effects that slight impurities exercise on these temperatures, and above all to heat conduction along the leads, as the couple is practically short-circuited by the salt near its surface. This is even more emphatically true when a couple is plunged bare into metal, which is bad practice even when the couple will stand it. The following list of salts is suggested, with considerable reserve as to the numerical values, some of which may be 10° C. or more in error:

$NaNO_3$	308° C.	$BaCl_2$	950° C.
KNO_3	336	K_2SO_4	1060
$Ca(NO_3)_2$	550	Na_2SiO_3	1088
KI	680	Li_2SiO_3	1202
KCl	780	Diopside	1391
✓ NaCl	800	Anorthite	1550
✓ Na_2SO_4	885		

Another sharply defined temperature which may be used is the transformation temperature of crystalline quartz at 575° C., obtained with a good quality of silica sand.

Still another method of calibration is by the comparison of the pyrometer readings with those of a standardized instrument in the same furnace. With the platinum couples and a porcelain-tube platinum-resistance furnace of 1.5 cm. diameter and 30 to 60 cm. long, results to 2 degrees or better may be obtained if special precautions are taken to insure constant temperature, such as inclosing hot junctions within a short platinum cylinder and passing them through notches in a platinum disk. When base-metal couples are compared with those of platinum, it is usually necessary to protect the latter from contamination from the former by inclosing the platinum wires and junctions in glazed porcelain or other suitable tubes. A better temperature distribution for the comparison of base-metal couples than is found usually in tube furnaces may be obtained by using large crucible furnaces in which are placed baths of mixed salts which may be stirred and contained in long iron crucibles.

Industrial and Scientific Applications. — The measurement of temperatures by thermoelectric couples has enhanced the accurate knowledge of a great number of high temperatures of which previously little or nothing was known. The earlier measurements were particularly numerous in the scientific and industrial investigations on iron. It was with the thermoelectric couple that Osmond and others, Roberts-Austen, Arnold, Howe, and Charpy made all their studies on the molecular transformations of irons and steels. The conditions of manufacture and of treatment of these metals have been improved by the introduction into industrial works of this method of high-temperature measurements.

We give below, as examples of the early use of the thermocouple, a series of determinations made by Le Chatelier in a number of industrial operations.

Steel. — Siemens-Martin open-hearth furnace:

Gas at the outlet of the gas generator	720°
Gas at the entrance of the regenerator	400
Gas at the outlet of the regenerator	1200
Air at the outlet of the regenerator	1000
Interior of the furnace during refining	1550
Smoke at the foot of the chimney	300

Glass. — Basin furnace for bottles; pot furnace for window glass:

Furnace	1400°
Glass in affinage	1310
Annealing of bottles	585
Rolling of window glass	600

Illuminating gas. — Gazogène furnace:

Top of furnace	1190°
Base of furnace	1060
Retort at end of distillation	975
Smoke at base of regenerator	680

Porcelain. — Furnaces:

Hard porcelain	1400°
China porcelain	1275

To-day, the use of the thermocouple in the most varied industries is so widespread that the above list could be indefinitely multiplied. It is not merely, however, in the determination of the temperatures entering into a great number of industrial operations that the thermoelectric pyrometer has paved the way for itself and for other types of pyrometer, but it is, above all, in the ability that is thereby given by such temperature measurements to control the quality of the products of these operations depending on temperature, and so permit the exact reproduction, within as close limits as is wanted, of any desired result, and to increase thereby enormously the efficiency of many industrial plants.

The use of the thermocouple in scientific investigations has been not less extensive or fruitful, and we have, for instance, what may be called a new science, or at least a new aspect of chemistry, namely, thermal analysis, which has grown up in recent years, based mainly on the interpretation of physicochemical phenomena at high temperatures by means of the indications of the thermocouple.

In the development of scientific metallurgy, again, the thermocouple has been almost the only temperature-measuring device which has been employed. These two generalizations are sufficient to indicate its secure position as an instrument of pyrometric research.

Conditions of Use. — Thermoelectric couples, as we have seen, may be divided for convenience into two general classes, the platinum-alloy couples and the base-metal couples, both of which are readily calibrated and easy to use. The former, by reason also of their small size and of the permanence and precision of their indications, are on the whole preferable to all other pyrometric methods for ordinary investigations, scientific or industrial, over the wide temperature range for which they are best adapted, or from 300° to 1600° C. We shall see, however, that when the highest accuracy is desired, or better than 1° C., the resistance thermometer of platinum may be given the preference to 900° C. from the very lowest temperatures, even over the thermocouple used with a potentiometer. The former also is somewhat more adapted for use with robust recording instruments. Above

1000° C., however, the platinum thermocouple is the only form of electric pyrometer which can be used with any considerable certainty; and attached either to a suitable direct-reading galvanometer or to an automatic recorder, this instrument is proving of great utility in the industries. It may also be wired readily for use in multiple on a single distant recording instrument, each couple also having its separate indicator beside it.

For temperatures below 600° C., there is gain in sensibility without serious loss in accuracy by substituting such couples as that of silver-constantan or copper-constantan, both of which can be kept small; and below 500° C. we reach the range of accurate mercury-in-glass thermometers. We have discussed elsewhere the precautions and methods of use both in work of precision and in technical work for the various types of couple.

The use of the base-metal couple is limited to the technical field, and even here great discernment has to be used to satisfy oneself that the couple in hand, with its accessories, is suitable for the use to which it is contemplated to put it. There are few base-metal couples which can be used safely above 1000° C., and some of them are of very questionable utility for any purpose.

We shall see that, even in the range for which it is best adapted, the thermocouple may in certain lines of work be replaced to advantage by still other methods, such for instance as the radiation and optical pyrometers.

CHAPTER V.

ELECTRICAL RESISTANCE PYROMETER.

Introduction. — In this method use is ordinarily made of the variations of electric resistance of a platinum wire as a function of the temperature; these variations are of the order of magnitude of those of the expansion of gases. The ratio of the resistances is 1.39 at 100°, and 4.4 at 1000°. As electrical resistances are measurable with great accuracy, this process of estimation of temperatures offers a very great sensibility, and applying exactly the law that connects the variation of resistances to that of temperature most excellent results may be obtained.

The electric pyrometer was proposed by Siemens in 1871 (Bakerian Lecture); it rapidly came into use in metallurgical works on account of the reputation of its inventor, but it was soon abandoned for reasons which will be given later. This method of temperature measurement was revived twenty years afterwards by Callendar and Griffiths, and has been growing in favor ever since, both in the laboratory and in the industries, especially in England, and more recently in America. It is perhaps of interest to note that in Cambridge, England, the resistance thermometer was first brought into a satisfactory condition as a physical instrument and its theory successfully worked out by Callendar and Griffiths; there it was first used in most delicate measurements of chemical phenomena by Heycock and Neville; and finally, the Cambridge Scientific Instrument Company were pioneers in the manufacture of instruments suitable for industrial and scientific use.

Work of Early Investigators.— *Siemens.*— The Siemens pyrometer consists of a fine platinum wire 1 m. long and 0.1 mm. in diameter, wound on a cylinder of porcelain or fire clay; the whole is inclosed in an iron tube, destined to protect the instrument from the action of the flames.

Siemens tried also, but without success, ceramic materials impregnated with metals of the platinum group.

To measure the resistance he employed either a galvanometer, for laboratory experiments, or a voltameter, for the measurements in works. In this latter case the current from a cell divides between the heated resistance and a standard resistance at constant temperature; in each one of the circuits was placed a voltameter: the ratio of the volumes of gas set free gives the ratio of the current strengths and thus the inverse ratio of the resistances.

Finally Siemens gave a formula of three terms connecting the electrical resistance of platinum to temperatures on the air thermometer, but without publishing the experimental data on which this graduation was based.

Experiment soon showed that the apparatus did not rest comparable with itself. A committee of the British Association for the Advancement of Science found that the resistance of platinum increases after heating. It would be necessary then to calibrate the apparatus each time that it was used. This change of resistance is due mainly to a chemical alteration of platinum, which is enormous when heated directly in the flame, less, but still marked, if placed in an iron tube, and which almost disappears if use is made of a platinum or porcelain tube. This increase of resistance may reach 15 per cent by repeated heatings to 900°.

Platinum being very costly and porcelain very fragile, it was impossible to use these two bodies in the industries, which alone at that time occupied themselves with measurements of high temperatures, and this method was abandoned completely during twenty years.

Callendar and Griffiths. — These savants revived this method for laboratory purposes; it seems the best for many kinds of work of precision to moderately high temperatures, on the condition of being assured of the invariability of the resistance of platinum.

Callendar found that clay helps to cause the variation of resistance, that the platinum wire becomes brittle on its support and sticks there; this action is probably due to impurities in the clay. With mica, on the other hand, which the wire touches only at the edges (the reel is made of two perpendicular slices of mica), there is perfect insulation without cause of alteration; but mica becomes dehydrated at 800° and then becomes very fragile.

All metallic solderings should be proscribed, for they are volatile and attack platinum.

Pressure joints (screw or torsion) are equally bad, for they become loose. One should use only autogenous soldering by the fusion of platinum.

Copper conductors should also be rejected, at least in the heated portions, on account of the volatility of the metal. A pyrometer with such conductors, heated during an hour at 850°, showed an increase of resistance of $\frac{1}{3}$ per cent.

Holborn and Wien. — These investigators made a very complete study of this alterability of platinum wires, in a comparison between the methods of measurement of temperatures by electric resistance and thermoelectric forces; they worked with wires of 0.1 mm. to 0.3 mm. diameter. They soon found that above 1200° platinum commences to undergo a feeble volatilization which suffices to increase notably the resistance of the very fine wires. Hydrogen in presence of silicious materials causes at about 850° a rapid alteration of the platinum.

Below are the results relative to wires of 0.3 mm. of a length of 160 mm.:

Wire α.	R at 15°.
At start	0.239 ohm
After heating red-hot:	
Twice in air at 1200°	0.238 ohm
Once in vacuo at 1200°	0.240 ohm
Once in H at 1200°	0.262 ohm
Once in vacuo at 1200°	0.253 ohm

Wire β.	R at 15°.
At start	0.247 ohm
After several days in hydrogen at 15°	0.246 ohm
After heating in hydrogen to 1200°	0.255 ohm

Wire γ.	R at 15°.
At start	0.183 ohm
After heating in air to 1250° (three times)	0.182 ohm
After heating in H to 1250°	0.188 ohm
After heating in H to 1250°	0.195 ohm

Wire γ heated to 1350° in an earthenware tube and in hydrogen became brittle; this result may be explained by a siliciuration of the platinum, for there is nothing observed if the wire is heated by the electric current in the interior of a cold glass tube, even in hydrogen. Similar experiments were made by the same observers with palladium, rhodium, and iridium. We shall return to this question of the constancy of the resistance of platinum.

Law of the Variation of Platinum Resistance. — Callendar and Griffiths have compared the resistance of platinum with the air thermometer up to 550° C.; they found that up to 500° the relation could be represented at least to 0.1° by a parabolic formula of three parameters. In order to graduate such a pyrometer it would be sufficient then to have three fixed points: ice, steam, and boiling sulphur.

They gave a special form to the relation; let p_t be the platinum temperature defined by the relation

$$p_t = \frac{R_t - R_0}{R_{100} - R_0} \cdot 100,$$

that is to say, the value of the temperature in the case in which the resistance varies proportionally to the temperature.

They then placed

$$t - p_t = \delta\left[-\frac{t}{100} + \left(\frac{t}{100}\right)^2\right].$$

It would appear as if this formula contained the single parameter δ; but in reality p_t includes two.

Substituting for p_t its value, we have

$$R_t = R_0 + \frac{(1+\delta)(R_{100} - R_0)}{(100)^2} \cdot t - \delta \frac{R_{100} - R_0}{(100)^3} \cdot t^2,$$

an equation of the form

$$R_t = R_0 (1 + at - bt^2),$$

which it is sometimes convenient to use. Callendar and Griffiths used their pyrometer before having standardized it against the air thermometer. Not being able to compute t, they provisionally computed the approximate temperatures p_t, and later determined the correction between t and p_t, after having sought the formula expressing the difference between these two quantities by means of a careful determination of the sulphur boiling point on the air thermometer. By extrapolation up to 1000° the points of fusion of gold and of silver were found quite near to those determined by other observers.

Harker, working at the National Physical Laboratory, England, has compared the readings of platinum thermometers, when reduced to the gas scale by the use of Callendar's difference formula, with the readings of thermocouples calibrated at the Reichsanstalt, and with the indications of an inglazed porcelain-bulb nitrogen thermometer at contant volume of the Reichsanstalt form. Specially constructed, compensated electric furnaces were used for heating.

As shown by the accompanying table, taken from one series of Harker's measurements, the agreement between the scales of the platinum-resistance and thermoelectric pyrometers was within 0.5° C. throughout the temperature range up to 1000°, although the gas pyrometer gave somewhat discordant results.

COMPARISON OF PYROMETRIC SCALES BY HARKER.

Temperature.			G − Pt.	G − Th.	P − Th.
Gas thermometer.	Thermocouple.	Pt thermometer.			
523.1	524.3	524.39	−1.3	−1.2	−0.1
598.5	597.8	597.62	+0.9	+0.7	−0.2
641.1	641.1	641.75	+0.6	+0.0	−0.6
776.7	775.5	775.13	+1.6	+1.2	−0.4
820.0	818.4	818.31	+1.7	+1.6	−0.1
875.0	875.4	875.24	−0.2	−0.4	−0.2
959.8	956.0	955.47	+4.3	+3.8	−0.5
1005.0	1004.4	1004.37	+0.6	+0.6	−0.0

A very careful direct comparison of the reduced indications of several platinum thermometers with the gas scale as furnished by the constant-volume nitrogen thermometer has also been made by Chappuis and Harker at the International Bureau at

Sèvres, and their results give further evidence that the indications of the platinum thermometer up to 600° C. can be sufficiently well expressed by Callendar's formula.

There is another method of comparison of temperature scales which is capable of great accuracy, namely, the determination on the several scales of the freezing and boiling points of a number of pure substances. This method has some decided advantages over the above method of comparison even in a most carefully compensated electric furnace. Heycock and Neville in England, and more recently Waidner and Burgess at the Bureau of Standards, have determined the freezing points of several pure metals in terms of the scale of the platinum thermometer standardized at 0°, 100°, and 444.70° C. (the boiling point of sulphur), and find that the freezing points so determined give temperatures on the gas scale as closely as the latter can be reproduced, as shown in the following table:

GAS AND RESISTANCE TEMPERATURE SCALES.

	Gas scale.		Resistance scale.	
	Holborn and Day.	Day and Sosman.	Heycock and Neville.	Waidner and Burgess.
Cd	321.7	320.0	320.7	321.0
Zn	419.0	418.2	419.4	419.4
Sb	630.6	629.2	630.1	630.7
Al	657.0	658.0	.....	658.0
Ag	961.5	960.0	961.9	960.9
Cu	1084.1	1082.6	1082.0	1083.0

These results confirm the view of the sufficiency of the Callendar difference formula for the most accurate work up to the upper limit of the safe use of the platinum-resistance thermometer.

Holborn and Wien have shown that at very high temperatures the interpolation formula is certainly inexact. The resistance seems to become asymptotic to a straight line, while the formula leads to a maximum evidently inacceptable; in their opinion it would be better represented by an expression of the form

$$R \cdot t = a + b\,(t + 273)^m.$$

Here are the results of two series of their experiments made on the same wire:

t Degrees.	R Ohms.	t Degrees.	R Ohms.
0	0.0355	0	0.0356
1045	.1510	1040	.1487
1193	.1595	1144	.1574
1303	.1699	1328	.1720
1395	.1787	1425	.1802
1513	.1877	1550	.1908
1578	.1933	1610	.1962

Using the Callendar formula and platinum wires, Petavel found the melting point of palladium to be 1489°, which Callendar and Eumorfopoulos found to be 1550°. This latter number is in exact agreement with the best determinations of this temperature.

Although the work of Holborn and Wien, as well as that of Tory and others, shows that the platinum-resistance thermometer made of fine wire cannot be depended upon to remain constant above 1000° C., yet, in the range from −200° C. to +1000° C., it serves as the most accurate, and, on the whole, most convenient method of measuring temperatures where great precision is required, and is particularly adapted for the delicate control of a given temperature.

Dickson has proposed the formula

$$(R + a)^2 = p\,(t + b),$$

in which a, b, and p are constants. It possesses the possible theoretical advantage over the Callendar formula of not requiring a maximum value for the resistance of platinum. This form, however, does not lend itself to the convenient graphical treatment applicable to the difference formula; and furthermore, for thermometers of pure platinum calibrated at three temperatures in the usual way, the Dickson formula does not reproduce the same temperature scale as the difference formula as shown by Waidner and Burgess, it giving, for instance, 1051° C. for copper instead of 1083° C. for calibration in ice, steam, and sulphur vapor.

Nomenclature. — To determine a temperature by means of a platinum thermometer, if the instrument has not been calibrated already in degrees, it is necessary to know the difference coefficient δ of the wire, which may be obtained by finding the platinum temperature pt at some known point, as the sulphur boiling point (S.B.P.), or by comparison with a calibrated instrument.

Callendar has suggested the following notation which seems convenient for platinum thermometry:

Fundamental Interval. — The denominator $R_{100} - R_0$ in the formula

$$pt = \frac{100\,(R - R_0)}{(R_{100} - R_0)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for the platinum temperature pt, represents the change of resistance of the thermometer between 0° and 100°.

Fundamental coefficient $= c =$ mean value of temperature coefficient of change of resistance between 0° and 100°:

$$c = \frac{(R_{100} - R_0)}{100\,R_0}.$$

Fundamental zero $= pt_0 = \frac{1}{c} =$ reciprocal of fundamental coefficient. It represents the temperature on the scale of the instrument itself at which its resistance would vanish.

Difference Formula. — The following form is the most convenient for computation:

$$D = t - pt = \delta \cdot \left(\frac{t}{100} - 1\right) \cdot \frac{t}{100}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Parabolic function expresses the vanishing at 0° and 100° of above formula, which becomes

$$t = pt + \delta \cdot p\,(t).$$

"S.B.P." Method of Reduction. — D is obtained very conveniently by determining R'', and thus pt'' at t'' = the boiling point of sulphur (= S.B.P.).

Resistance Formula. — The parabolic difference formula is equivalent to assuming

$$\frac{R}{R_0} = 1 + at + bt^2, \qquad \qquad (3)$$

where

$$a = c\left(1 + \frac{\delta}{100}\right), \quad b = -\frac{c\delta}{10{,}000};$$

or

$$\delta = -\frac{b \cdot 10^4}{a + b \cdot 10^2}.$$

Graphic Method of Reduction. — An easy way to reduce platinum temperatures to the gas scale is to plot the difference $t - pt$ in terms of t as abscissas, and to deduce graphically the curve of difference in terms of pt as abscissas. This is most convenient for a single instrument up to 500°.

Other methods have been used by Heycock and Neville and by Tory.

Difference Formula in Terms of pt. —

$$t - pt = d'\left(\frac{pt}{100} - 1\right)\frac{pt}{100} = d'p\,(pt). \qquad (4)$$

This formula is to be used only where a high degree of accuracy is not required. The value of d' may be determined from S.B.P., or approximately

$$d' = \frac{\delta}{(1 - 0.077\,\delta)}.$$

Construction of the Platinum Thermometer. — Callendar first devised a satisfactory and perhaps the most commonly used form of platinum thermometer, in which the platinum wire is wound on two strips of mica set crosswise. In Fig. 61 is shown a laboratory form of Callendar's potential terminal thermometer used at the Bureau of Standards in precision work to 1100° C. The heavy copper head insures a minimum of thermoelectric effects at the platinum-copper junctions, and provision is made for air cooling of the head, which is an advantage for work at the highest temperatures. The junctions of the leads to the platinum coil are easily made by arc soldering, using platinum as one terminal and a graphite pencil as the other. No material other than platinum should enter into joints to be heated. Forms of mica supporting frame are shown in Fig. 62.

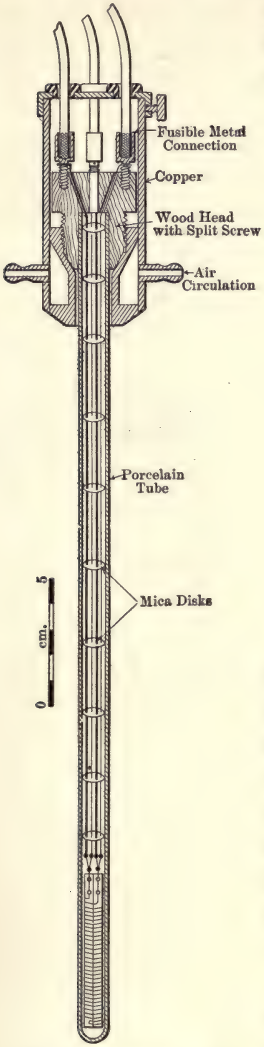
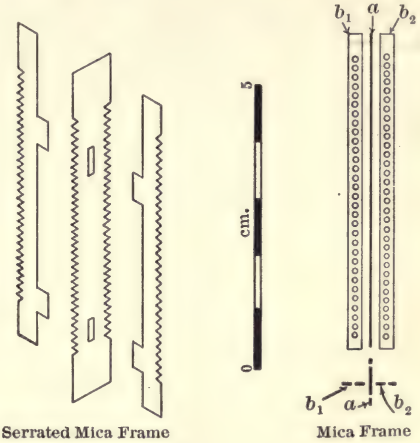


Fig. 61. Resistance Pyrometer, Laboratory Type.



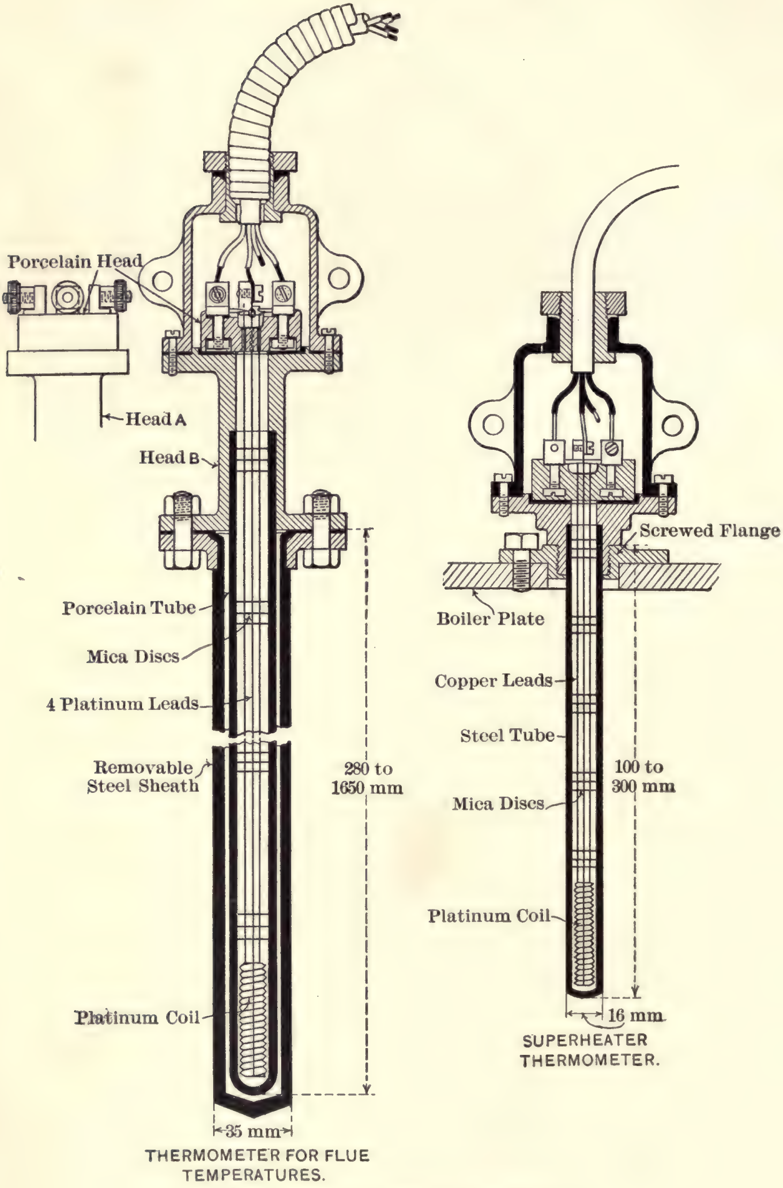
Serrated Mica Frame

Mica Frame

Fig. 62. Mica Frames.

Various modifications of the above design are used in the industrial forms, they being in general so arranged as to secure the maximum of protection and robustness to the platinum coil. Mica frames are sometimes replaced by steatite by Leeds and Northrup except for the highest temperatures. Industrial types of mounting used by the Cambridge Company are shown in Fig. 63.

The outer containing tubes for industrial instruments are preferably of metal, such as nickel or iron, over a quartz or porcelain tube, the actual material of the sheath depending, however, on the use to which it is to be put.



THERMOMETER FOR FLUE TEMPERATURES.

SUPERHEATER THERMOMETER.

Fig. 63. Types of Industrial Mounting.

For use at very high temperatures, Leeds and Northrup have designed the form of potential lead thermometer shown in Fig. 64. Heavy wire (0.6 mm.) is used in the coil, which is freely suspended and therefore not subject to strains on cooling. Due to its very low resistance, special precautions have to be taken in the temperature measurements to secure sensibility. Such heavy-wire thermometers will change their constants very much less than those of fine wire when heated to high temperatures. Thus Waidner and Burgess found that heating them for several hours to 1200° or 1300° C. changed the zero reading by only a few tenths degree, after they had been once annealed at 1300° C.

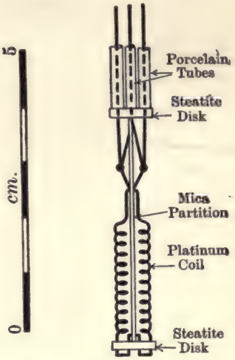


Fig. 64. Freely Suspended Coil.

In order to secure an instrument of small volume and at the same time satisfactorily protect and rigidly mount the platinum coil, Heræus has devised the form shown in Fig. 65, in which the platinum coil is embedded in fused quartz glass.

The behavior of this type of thermometer, with wires of 0.05 to 0.15 mm., has been studied at the Reichsanstalt. The effect of embedding in quartz is to decrease the value of a (equation (3), page 202) and increase the value of δ. As compared with wires mounted in the usual way, and receiving the same heat treatment, the change in the constants is very great for these thermometers. For the former, a decreased by 0.45 per cent and δ by 0.65 per cent; for the latter, the changes were 1.7 per cent and 6.7 per cent respectively.

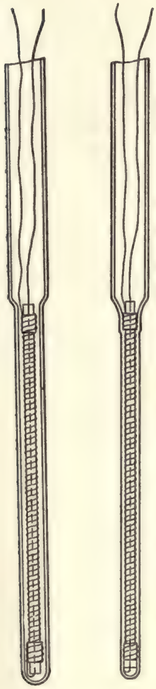


Fig. 65. Mountings in Quartz.

Where very great rapidity of action is desired the form of construction shown in Fig. 66, due to Dickinson, may be used in certain cases, the metallic parts being preferably all of platinum where great permanence is desired, and the insulation of mica strips.

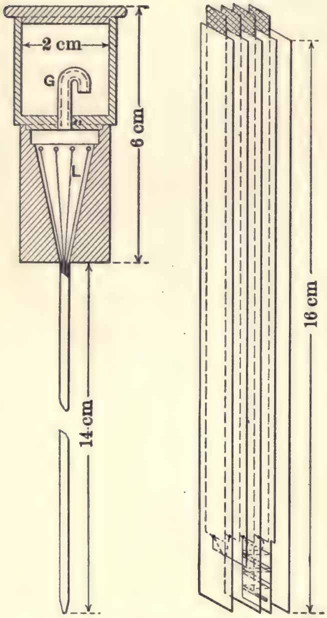


Fig. 66. Thermometer of Small Lag.

Where platinum thermometers are to be used with a definite form of measuring apparatus, or where several such thermometers are to be used with a single bridge, recorder, or other indicating or registering device, it is convenient to have them all adjusted to exactly the same resistance at zero and of the same fundamental interval, and so make them interchangeable. This is done by several firms by means of auxiliary manganin coils set into the thermometer head.

Choice of Size of Wire. — Regarding the choice of the diameter of wire to use in constructing a thermometer coil of given resistance, there are several points to consider besides the current-carrying capacity without undue heating of the coil, which is in favor of the heavy wire; such as the greater temperature lag, heat conduction along the leads, and excessive size of the thermometer coil, which, together with the cost, are the main inconveniences of heavy wire; and liability to strains, fragility, and greater evaporation, which limit the use and precision of too small wire. It is easy to get enough current sensibility, constancy of resistance, and robustness with wires of 0.15 to 0.20 mm. diameter except for very low-resistance pyrometers, 2 ohms or less, which are to be avoided, save for work at very high temperatures, as taxing too severely the sensitiveness of ordinary forms of measuring apparatus.

Precautions in Construction and Use. — The platinum thermometer, as usually constructed, is a fragile instrument in spite of its appearance of robustness when encased in a metal tube, therefore careful handling is required. To avoid breaking from sudden heating when porcelain or similar containing tubes are used, the pyrometer should be installed in advance in the furnace, or preheated in a muffle if it is necessary to introduce it into the hot furnace. It is necessary, also, to heat a sufficient length of the stem in the furnace in order to avoid the effect of heat conductivity, which would prevent the thermometer spiral from taking up the temperature of the space in which it is immersed. Platinum is readily attacked and its resistance changed by contact with most substances, including many vapors and gases, so that the thermometer coil must be carefully shielded by materials impervious to the atmosphere in which it is placed, such as porcelain glazed on the *outside*. As platinum changes its nature with heating, and as the frame on which the coil is wound may permanently change its dimensions, especially if mica is used, the thermometer before calibration should be annealed at a temperature higher than that at which it is to be used. A platinum thermometer will change its readings with time the more rapidly, the higher the temperatures at which it is used; therefore, in order to control its constancy, it is necessary to take its reading occasionally at some known temperature, as the ice or steam point. Well-shielded, pure platinum wound on a frame that does not contaminate the wire will change its constants with use less than does impure platinum, so that it is highly desirable to use only the purest of platinum in the construction of pyrometers. Even with pure platinum, however, in work of great precision, it is necessary to recalibrate occasionally, and when temperatures above 1000° C. are measured frequently this operation becomes very onerous. Great care has to be exercised, and this should be especially emphasized for industrial as well as scientific installations, to secure a proper insulation of all electrical circuits.

Methods of Measurement. — It is evident that most of the ordinary methods for the measurement of resistance may be used in platinum thermometry, but in practice only a few of these methods have been applied to temperature measurements, although there is a tendency at the present time, in the solution of specific-temperature problems, to take advantage of the peculiarities of less usual methods both for work of high precision in the laboratory and for industrial applications. Thus, in addition to the ordinary slide-wire and dial Wheatstone bridge methods, the Kelvin double bridge is sometimes used with pyrometers of very low resistance, for which this method is particularly adapted. Potential terminal and differential galvanometer methods are also used in precision work, and for industrial practice several deflection methods have been developed for the direct reading of temperatures on a galvanometer scale.

Compensation for Pyrometer Leads. — There is one characteristic in the measurement of a resistance coil used as a pyrometer that distinguishes it from an ordinary resistance measurement, namely, that in the case of the pyrometer coil there is a region of great temperature gradient from the coil to the measuring apparatus, so that it becomes imperative to eliminate the variable resistance of the leads to the pyrometer coil — a resistance that varies both with the depth of immersion of the coil and with its temperature. There are several ways of effecting the necessary compensation of this variable lead resistance, and they will be described under the several headings.

Three-lead Thermometer. — This was the form originally given to the instrument by Siemens in 1871, and it is used in the construction of apparatus suitable for industrial use by Siemens and Halske and by Leeds and Northrup.

In the Siemens method (Fig. 67), the thermometer coil P forms one arm of a Wheatstone bridge, of which the others are r_1, r_2, and R, when from the principle of the bridge, if the galvanometer G remains undeflected, $P = R\frac{r_2}{r_1}$, neglecting the leads.

The compensation for the variable resistance of the thermometer leads is effected in the following manner: The lead aa', of the same material as the thermometer coil P to avoid thermoelectric effects at their junction, is constructed to be as exactly equal as possible electrically to the similar lead bb'. The lead *aa′* is in the *P* arm of the bridge and the lead *bb′* is put in the *R* arm by means of the auxiliary lead *c′b* of the same material as *P*.

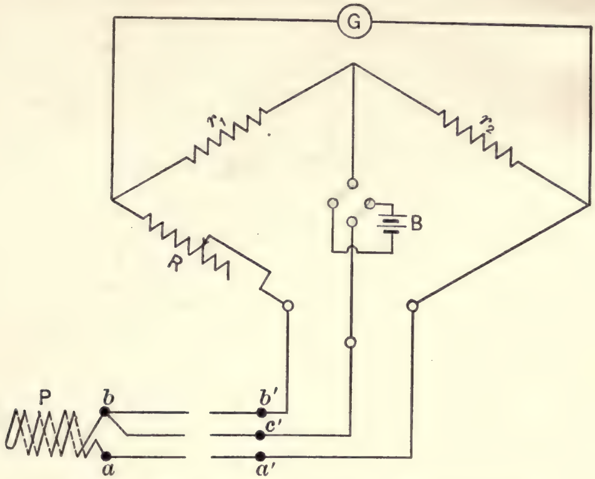


Fig. 67. Three-lead Compensated Thermometer.

This lead *c′b* may be put in the battery circuit as shown, or in the galvanometer circuit if preferred. It is not necessary to adjust *c′b* to any particular resistance, so that fine wire may be used for it. With this arrangement, therefore, the resistance of the thermometer remains apparently constant for a given temperature whatever its depth of immersion and whatever the temperature gradient along the leads *aa′*, *bb′*, so long as it is the same for both.

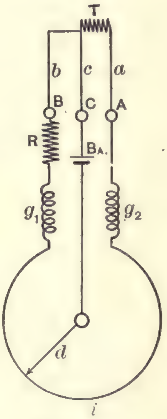


Fig. 68. Use of Differential Galvanometer.

The three-lead compensated thermometer may also be used with a differential galvanometer. Fig. 68 shows the principle of such an arrangement for an instrument of Leeds and Northrup. The slider *d* is set on the slide wire *i* in such a position that the current from *B* divides equally between the circuits $b + R + g_1$ and $T + a + g_2$, of which g_1 and g_2 are the two differential galvanometer coils. If the resistance

R remains fixed, the changes in temperature of *T*, the thermometer coil, may be read directly in degrees on the slide wire if desired. The compensation by means of the leads *a*, *b*, *c* is effected as before. The arrangement used by Siemens and Halske is shown in Fig. 69. In Fig. 70 is shown a system of wiring for four thermometers of the Siemens type and used with a single indicator.

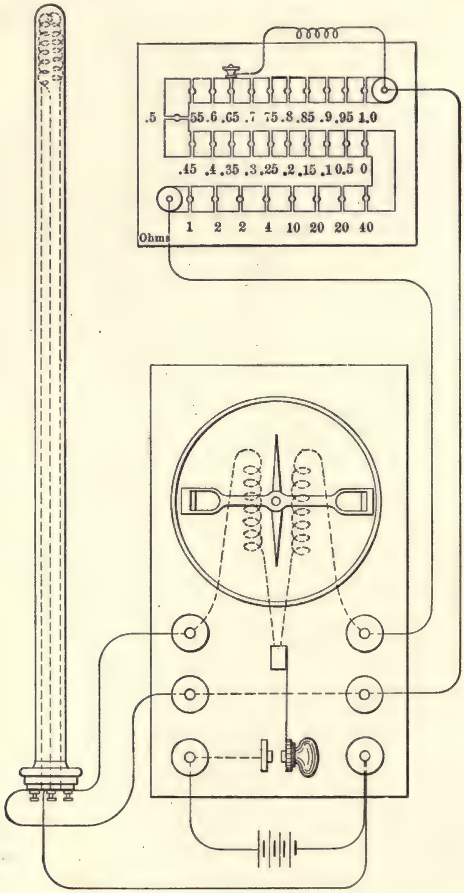


Fig. 69. Thermometer of Siemens and Halske.

For work of great precision, this method is of course capable of elaboration and refinements, as in the calorimetric measurements of Jäger and Steinwehr, who, however, used a four-lead thermometer.

Four-lead Thermometer. — There are four ways in which the four-lead compensated thermometer of Callendar and Griffiths has been used, namely, the Wheatstone and Kelvin bridge, the potential terminal, and the differential galvanometer methods.

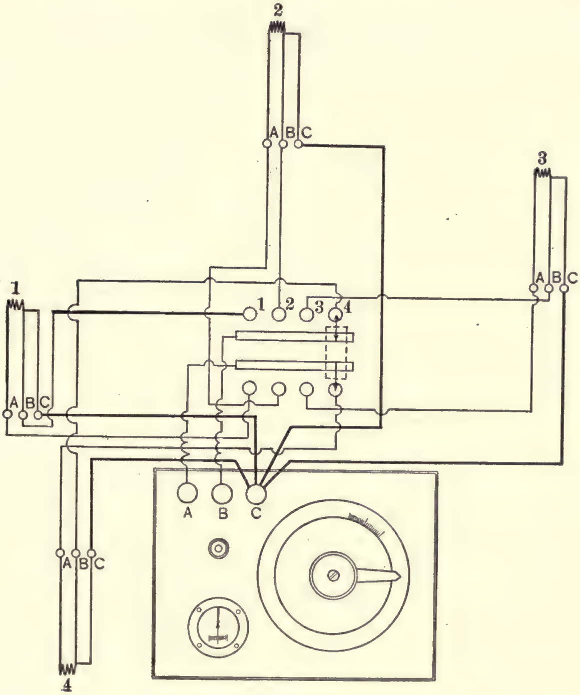


Fig. 70. Four Thermometers with One Indicator.

The *Wheatstone bridge method* is illustrated in Fig. 71, from which it is seen that the compensating leads are inserted in one arm R of the bridge and the thermometer leads in the other. It is necessary that all four leads be as nearly as possible of the same length, diameter, and material. For work of great accuracy it is necessary to take all the precautions which obtain in exact resistance measurements, and in particular the elimination of thermoelectric effects and uncertainties in the exact value of the ratio coils.

Precision Bridges. — In Fig. 72 is shown diagrammatically the important features of a bridge designed and in use at the Bureau of Standards, constructed by Leeds and Northrup, and capable of measurements to 1 in 100,000, and connected, in the figure, for use with a four-lead thermometer. This bridge can also be used, however, with a three-lead thermometer. Some of its characteristics are possibility of reversal of all circuits, the interchangeability of the ratio coils, mercury contacts for the higher resistances to eliminate contact resistances, a device due to Waidner consisting in a split ohm shunted across three dials to give rapidity of setting for final adjustment, and the ability to test the bridge without other accessories. The bridge is oil-immersed and kept at constant temperature by thermostatic control, and all coils are of seasoned manganin, which for the very highest precision should be sealed air-tight separately to avoid effects of humidity even beneath the oil. As galvanometer, a very sensitive form of d'Arsonval, due to Weston, is used, and

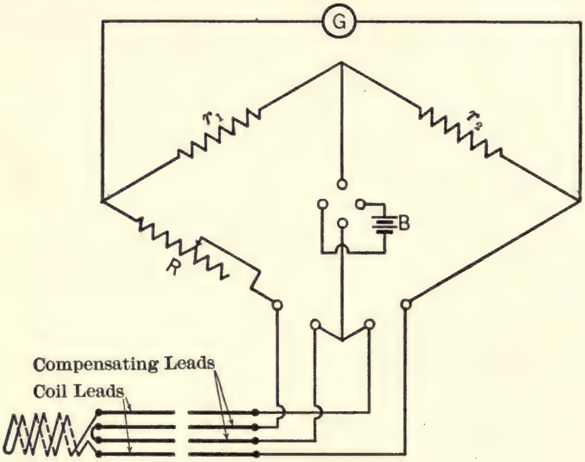


Fig. 71. Four-lead Compensated Thermometer.

as battery one to three dry cells. The thermoelectric key may be dispensed with and a single contact key put in the battery circuit, with a variable resistance to replace the usual galvanometer shunt for varying the sensibility.

Another form of the Callendar and Griffiths self-testing bridge, designed primarily for use with resistance thermometers of a fundamental interval of one ohm, is constructed by the Cambridge Scientific Instrument Company. To eliminate temperature variations in this bridge, not only the coils but the bridge wire and all contacts are oil-immersed; and it is capable of reading platinum temperatures, in the latest model, to better than 0.01° C. by direct reading on the scale of the bridge wire, when a galvanometer of suitable sensibility and resistance is used, such as a Broca instrument of 10 ohms.

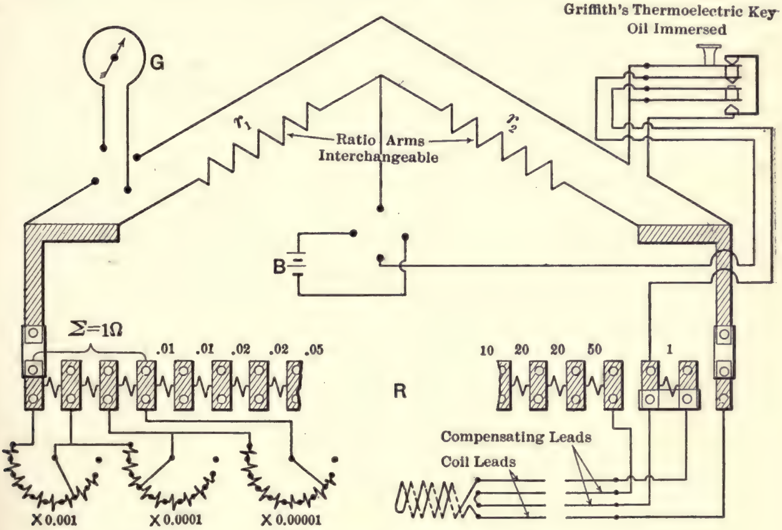


Fig. 72. Thermometer Bridge of the Bureau of Standards.

The principle of the construction and wiring of this bridge is shown in Fig. 73, in which R_1 and R_2 are ratio coils of 10 ω each, which should be interchangeable, BC the balance arm, adjustable by nine manganin coils AR and the slide wire s, while DC is the thermometer arm. *P* and *C* are the thermometer and compensating leads respectively.

The unit of the bridge is one degree on the platinum scale (page 201), and this corresponds to 0.01 ω for a F.I. of 1 ω in the thermometer. This bridge possesses many mechanical excellencies, such as a special form of combined plug and mercury contact, protection from mercury, and a convenient form of vernier and slide wire.

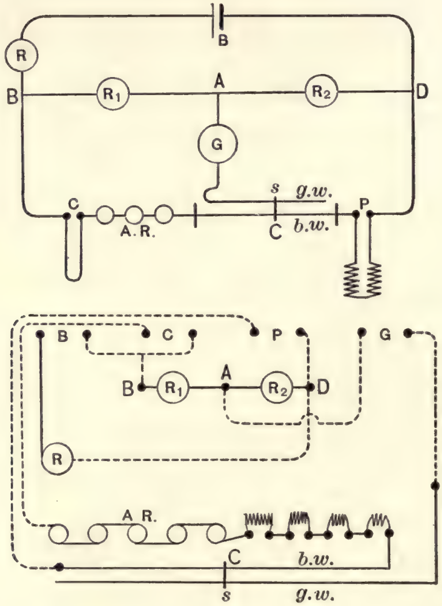


Fig. 73. Callendar and Griffiths Bridge.

The resistance of the *potential terminal thermometer* is determined by sending the same current from a storage battery through the thermometer and a known resistance in series, and measuring the potential drop by means of a potentiometer (page 138), first across the known resistance and then across the thermometer coil. This method of measurement for accurate work is illustrated in Fig. 74, which shows a rheostat and milliammeter in the circuit for adjusting the measuring current. The mercury-contact resistance box may be adjusted to within 0.01 ohm of the thermometer, thus eliminating potentiometer errors. This box may of course be replaced by a single-standard resistance, in which case an accurate calibration of the potentiometer is required.

The current leads for this type of thermometer do not have to be adjusted to equality, and the potential leads may be of fine wire, as may also the current leads, but still keeping the thermometer sufficiently robust, so that errors due to heat conduction along the leads need not creep into the measurements.

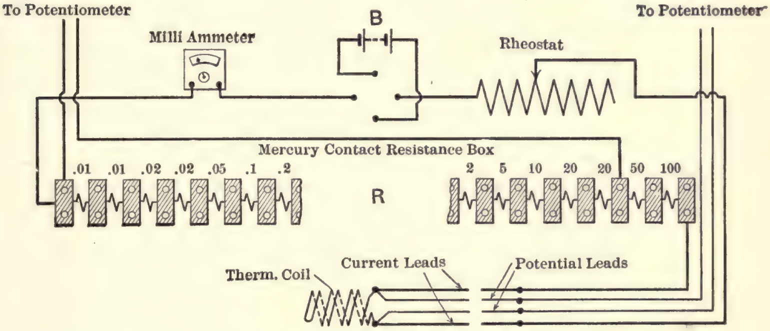


Fig. 74. Potential Terminal Thermometer of Precision.

The Kelvin Bridge. — The principle of this method of measuring resistances is shown in Fig. 75, in which S is an adjustable resistance, x the unknown, and the others are such that, by construction, $\frac{a}{b} = \frac{a_1}{b_1}$, when $x = \frac{a}{b} S$ for no current in the galvanometer. This method of bridge design, accompanied by a sufficiently sensitive galvanometer, permits the measurement of 0.01 ohm to be made with about the same precision as 100 ohms by the usual bridge methods, and is therefore particularly well adapted for resistance thermometers which are to be used at very high temperatures, because such instruments must be made of wire of large diameter, and therefore of low resistance, in order to avoid changes in their constants due to heating. The Kelvin bridge method permits cutting down the amount of platinum in the pyrometer, an advantage both in cost and in volume of the instrument.

Leeds and Northrup made a potential point indicator (Fig. 75 A), with slide wire for use with a heavy-coil low-resistance thermometer carrying a current of 0.3 ampere. The extension coils and slide wire may be graduated in degrees of temperature for any given thermometer. The high values (520 ω) of a and a' (Fig. 75), necessary to eliminate resistance changes in the potential leads, require that the galvanometer used shall have a greater sensibility than can easily be gotten in a portable pointer instrument. The type of galvanometer is the same as that required for high-precision Wheatstone bridge work with proper adjustment of critical external resistance.

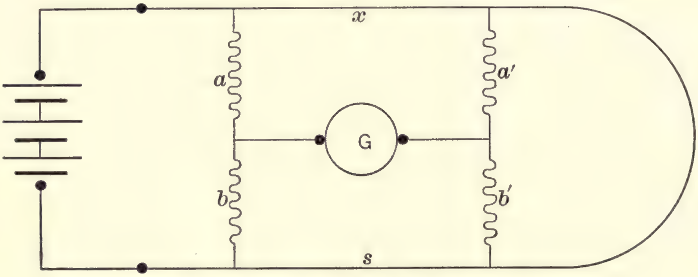


Fig. 75. Principle of Kelvin Bridge.

Sensibility. — The sensitiveness of the measurements in resistance thermometry is that of the very great precision attainable in resistance measurements, or it may be better than 1 in 100,000, or about 0.001° C. for a high-temperature thermometer whose resistance at 0° C. is from 3 to 25 ohms, if proper precautions are taken. The factors limiting the sensibility of resistance measurements in the Wheatstone bridge method, for example, and which are inherent in thermometric work, are the practical necessity of using a 1 : 1 ratio, required for the lead compensation; the need of keeping the current through the thermometer coil so low as not to raise its temperature unduly; and finally, the sensibility of the galvanometer. Due to the first and second of these conditions, the ordinary rules for the Wheatstone bridge do not apply without modification, and fortunately the limitations they impose may very largely be overcome by properly choosing the constants of the thermometer and galvanometer. It should be remarked that, with the d'Arsonval or

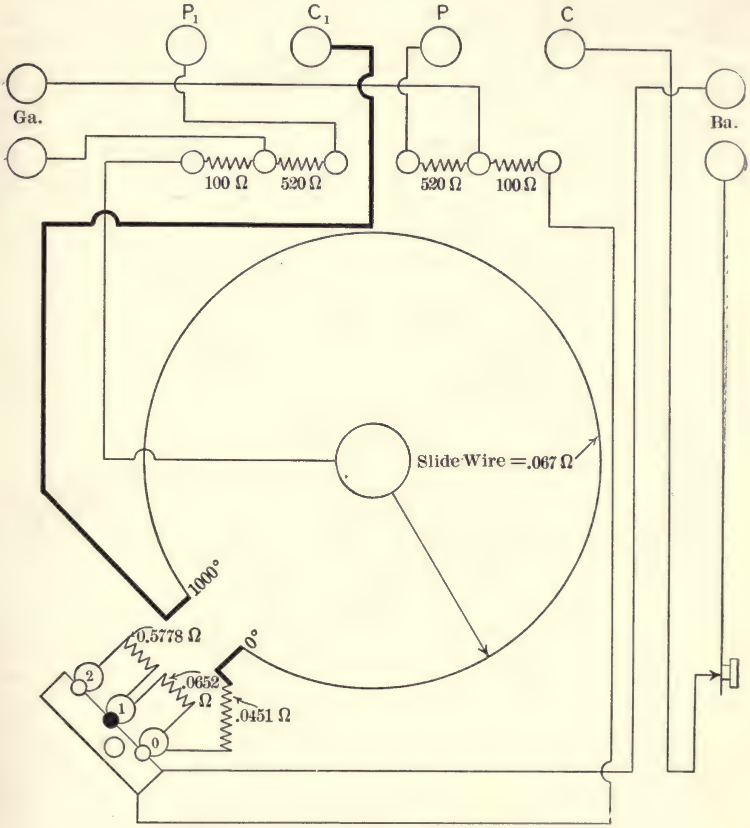


Fig. 75 A. Potential Point Indicator.

moving-coil galvanometers of very great sensibility and of practically constant zero which are available to-day, the question of the realization of sufficient sensibility is of distinctly secondary importance in accurate work. In the case of recording instruments, when in general a less sensitive instrument must be used, some attention has to be paid to the matter, and particular care has to be taken here to so arrange as not to overheat the thermometer with the larger currents required by such galvanometers. For the maximum current through the galvanometer and the minimum through the thermometer coil, with a battery of negligible resistance, the bridge should be arranged as follows, as shown by Callendar: " Connect the battery so as to make the resistance in series with the thermometer greater than the resistance in parallel."

Direct-reading Thermometers. — There have been in recent years a considerable number of direct-reading resistance pyrometers devised by several manufacturers. We shall be able to call attention to only a few typical instruments, which are, of course, of interest mainly in technical practice. A principle commonly made use of in some of its modifications is that of the *ohmmeter*, in which a variable resistance, that of the thermometer, is balanced against a fixed resistance by means of the deflection of a galvanometer coil carrying currents from circuits shunted around the two resistances in question. Such deflection instruments are constructed by Paul, Hartmann and Braun, Carpentier, Leeds and Northrup, and others.

The Harris Direct-reading Resistance-thermometer Indicator, manufactured by Mr. Robert W. Paul of London, indicates temperatures directly by the movement of a pointer over a scale; moreover its accuracy is independent of the battery or supply voltage used.

In principle it is a two-coil ohmmeter, or coil-controlled galvanometer; the requisite sensitivity to the small changes in resistance, which are utilized in platinum thermometry, is attained by making the action of the deflecting coil differential.

The differential windings of the deflecting coil are respectively connected in shunt with the platinum thermometer and a resistance equivalent to that of the thermometer at any desired temperature, dependent upon the part of the temperature scale at which it is desired to work. The control coil of the ohmmeter system is connected in shunt with a resistance suitably chosen to give the required sensitivity. These combinations are connected in series. Hence, on the passage of an electric current, the forces due to the windings are proportional to the resistances they respectively shunt.

In the accompanying vector diagram, the platinum thermometer is assumed to have a Fundamental Interval of one ohm and to be brought up to a resistance of three ohms at 0° C., by means of a resistance which has no temperature coefficient, suitably introduced into the circuit. This enables the thermometers to be made electrically interchangeable with each other.

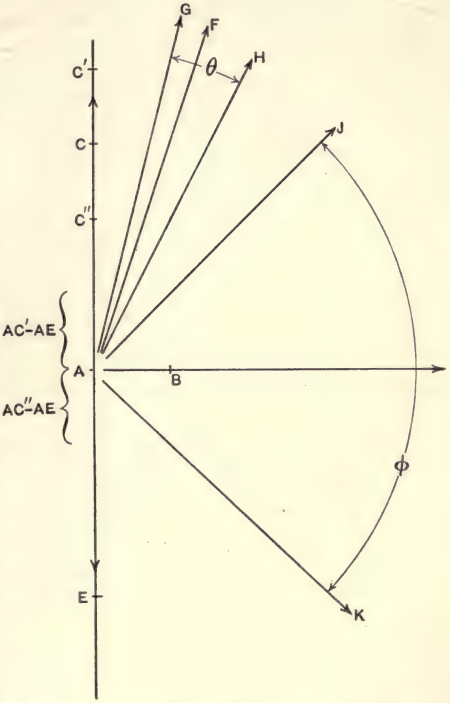


Fig. 76. Vector Diagram for Ohmmeter.

Considering first the case of an ohmmeter system without the differential winding of the deflecting coil, let AB represent the controlling force of the ohmmeter system (proportional to the control-coil shunt referred to above, and in this instance taken as one ohm); and let AC represent the deflecting force with a platinum thermometer of one ohm Fundamental Interval at 0° C. The pointer of the instrument will then take up the position AF.

Suppose the temperature of the thermometer is raised to 100° C.; the deflecting force now increases by the amount of CC' (proportional to one ohm) and becomes equal to AC', causing the pointer to set along AG. Similarly, if the thermometer drops to $-100°$ C., the position taken up by the pointer is along AH, giving an angle θ for 200° C. variation.

If, however, the deflecting coil be wound differentially, and a current equal to that producing the deflecting force AC be passed through the other winding in such a direction that its effort is in opposition to AC, introducing the vector AE, the initial position of the pointer will be along AB, and a variation CC' in the vector AC gives a resultant AC'' and causes the pointer to set along the line AJ. Similarly, should AC decrease by an amount equal to CC', the resultant deflection is on the opposite side of the initial position, and the pointer takes up the position AK, giving the large angle ϕ for the change in the thermometer resistance equal to that which only gave the angle θ with a nondifferential arrangement. It will be noted that AE may be given a value equal to AC at any required temperature of the platinum thermometer, the position of the pointer at such temperature lying along AB and covering the same angles as before for the same ohmic variation in the thermometer resistance. By simultaneously varying the vector AB the angle ϕ may be kept true to gas-scale temperature. It is thus possible to construct a multiple-range instrument.

The accompanying diagram, Fig. 77, shows the scheme of connections for such an instrument. One of the differential windings (X in the figure) is shunted with a platinum thermometer, the other winding S being shunted with a resistance s, which is made variable so as to equal the resistance of the thermometer at certain fixed temperatures. The control coil of the ohmmeter system is also shunted with the resistance d, the value of which is determined by the degree of sensitiveness required, and may be made variable with s. These shunted windings are connected in series, and the circuit is completed through a battery and switch.

In this arrangement, since the currents in the ohmmeter system windings depend upon the resistance of the platinum thermometer, *s* and *d* respectively, the value of *s* may be taken as the vector *AE*, increasing by steps equal to the rises in resistance of the platinum thermometer for each range of temperature. The platinum thermometer represents the vector *AC*, *AC′*, etc., while *d* represents *AB*. This is made variable with *s* in order that the instrument shall read in gas-scale degrees on all ranges, and its values are calculated in accordance with Callendar's formula for the platinum thermometer.

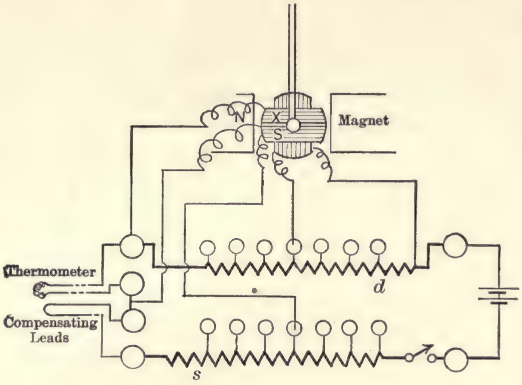


Fig. 77. Harris-Paul Indicator.

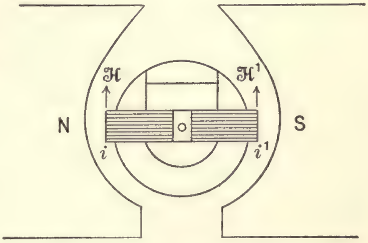


Fig. 78. Logometer Coil.

The Logometer and Ratiometer. — Messrs. Carpentier and Joly have also proposed the construction of a deflectional-resistance pyrometer based on the use of the logometer, an apparatus designed for the measurement of the ratio of two currents. This is shown in plan in Fig. 78, where two oppositely wound coils, similar to those of a d'Arsonval galvanometer, are mounted by double pivot in the unsymmetrical field of a permanent magnet *NS*. If the two coils have the same number of turns, we have $iH = i'H'$, and since the electromagnetic force of each coil is directed toward a weaker field, the final position of the coils will be stable and will depend only on the ratio of the two currents i and i' in the coils.

For the measurement of resistance, the circuit, in one of its simplest forms, is arranged as shown in Fig. 79, the logometer coils being shunted, one about a manganin resistance r and the other about the platinum thermometer of resistance p; when if s and s' are the coil resistances, their currents are $\frac{ir}{s}$ and $\frac{ip}{s'}$, where i = current in principal circuit, and their ratio is $\frac{p}{r} \cdot \frac{s}{s'}$, a quantity whose variations depend only on p, the resistance of the platinum thermometer, neglecting any variations in the resistance of leads to the logometer coils. The logometer dial, over which moves a pointer attached to the moving coils, may therefore be graduated directly in degrees of temperature. The readings of the instrument are independent of the value or of variations in the current i. Measurements may be taken with alternating currents, and when the manganin and platinum coils are noninductively wound, the readings will be independent of changes in voltage and frequency. This instrument may be arranged to develop relatively powerful directing couples and is therefore readily rendered recording.

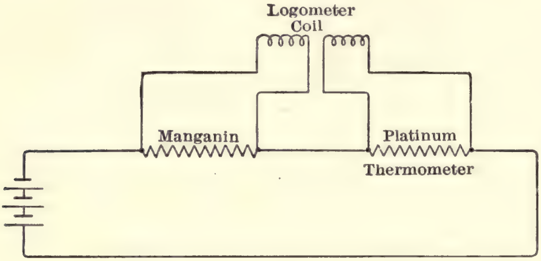


Fig. 79. Simple Logometer Circuit.

Northrup's ratiometer, similar to the preceding, is also an adaptation of the deflection-ohmmeter principle to temperature measurements. Northrup makes use of the three-lead thermometer with connections as shown in Fig. 80, in which C_1 and C_2 are two flat coils mounted on a damped movable system between the two crescent-shaped pole pieces of a permanent magnet. This instrument, which is made in a compact form and read by an attached microscope, can be made sensitive to about 0.1° C. and constant to better than 2° C.

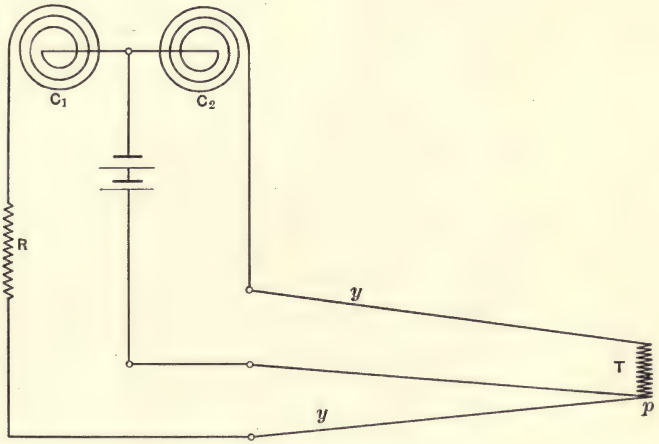


Fig. 80. Northrup's Ratiometer.

The Cambridge Deflectional Instrument. — The Cambridge Scientific Instrument Company also have recently devised a deflectional method for the measurement of temperature with resistance thermometers, in which the temperature is indicated by the "out-of-balance" current in a Wheatstone bridge, provided with compensating leads; the arms of the bridge are all fixed resistances except the one which forms the resistance thermometer. As designed, provision is made for exactly setting the zero of the indicator for a balance of the bridge, for adjusting the current to give the required deflection for the temperature range, and is provided with an "ice coil" for balancing the thermometer at 0° C.

The Whipple indicator shown in Fig. 81 is a dial instrument using the Wheatstone bridge principle. The galvanometer needle has to be brought to rest by turning a knob, when the dial reading gives temperatures directly.

The Leeds and Northrup Indicators. — This firm has brought out several patterns of balance and deflection indicator instruments based for the most part on the use either of the differential galvanometer (page 209) or the Kelvin bridge (page 215).

A very convenient deflection indicator with adjustable scale is shown in Fig. 82. The dial may be set to any desired temperature, and the position of the deflector needle indicates how much higher or lower the furnace is than the required temperature. The deflector has a very open scale, permitting readings to be taken from a distance. The workman has to concern himself only with deflections of the needle from the vertical. The accuracy is independent of voltage fluctuations, and the instrument may be run, if desired, from the ordinary lighting circuit. Temperature intervals as small as two degrees are readable.

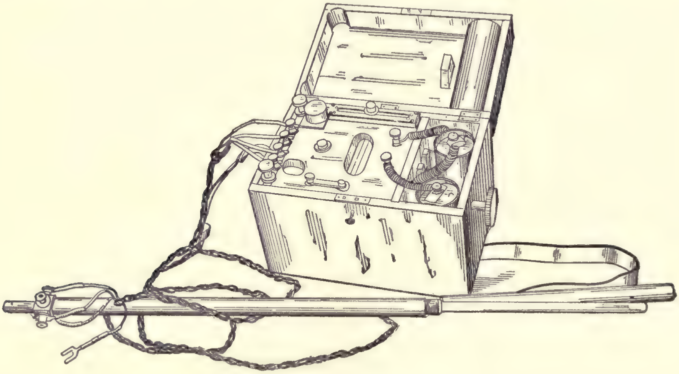


Fig. 81. Whipple Indicator.

Calibration. — For platinum thermometers which are to be used with some form of calibrated resistance-measuring apparatus, such as described above, it is only necessary, in order to calibrate the thermometer, to take its readings at three temperatures, as at the ice point, the steam point, and the boiling point of sulphur, when, if the wire is of pure platinum, the temperatures found by using Callendar's method of computation (see page 201) will be correct to as close as they are known in terms of the gas scale to 1100° C.

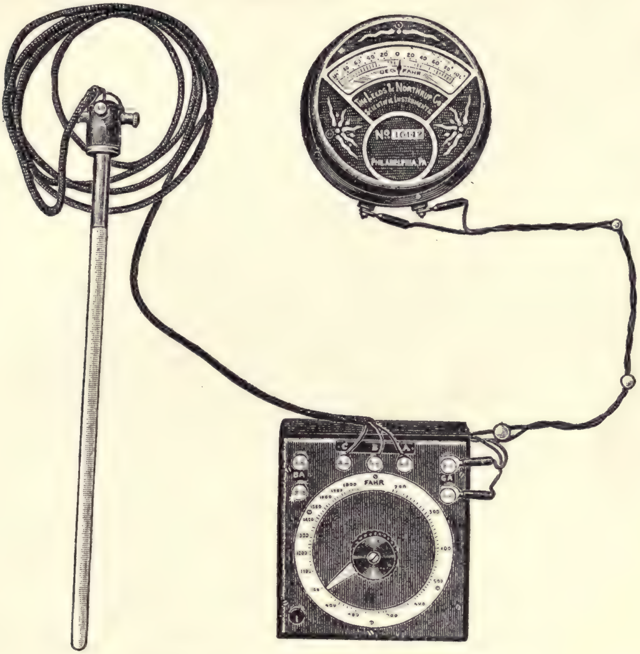


Fig. 82. Deflection Indicator of Leeds and Northrup.

There is advantage in using a fourth calibration point, as the silver freezing point, or that of Ag_3-Cu_2, in calculating the value of δ (page 201) for impure wires that are to be used at high temperatures. For the whole range of temperatures with such a wire, both the sulphur and silver points may be obtained, when δ takes the form $a + bt$.

For thermometers to be used with direct-reading temperature indicators, it is necessary to compare their readings with those of a standard at several temperatures, preferably in a resistance furnace of the Heræus type. This second method of calibration is usually less accurate than the first. Methods of realizing experimentally the sulphur point and other fixed temperatures will be described in Chapter XI on Standardization.

The platinum thermometer may be, and should be, for technical work, so constructed as to read directly in platinum degrees, or still better in degrees of temperature. This method saves much time and chance of mistake. The calibration curve, once made for an instrument, serves indefinitely, with occasional checking up if used at high temperatures; so that in spite of the appearance of complications in this method of measuring temperatures, actually in practical use the determination of a temperature on the normal scale by the platinum thermometer is the affair of a few seconds only.

Reduction Tables. — In the Appendix are given tables for the reduction of platinum temperatures to centigrade temperatures for wires of pure platinum, correction tables for wires of impure platinum, and other auxiliary tables.

Some Results Obtained. — There is a remarkable agreement among the fixed points obtained by several observers using the platinum thermometer, for observations extending over twenty years, as shown in the following tables, in which all the observations were obtained by calibrating the platinum thermometer in ice, steam, and sulphur vapor, the temperature of this last being here taken as 444.70 on the constant-volume nitrogen scale, the value best representing the work of these observers except Holborn and Henning.

SCALE OF RESISTANCE THERMOMETER.

	Boiling Points.	
	Naphthaline.	Benzophenone.
Callendar and Griffiths (1891)	217.97°	305.89°
Travers and Gwyer (1905)	218.07	305.87
Holborn and Henning (1908 and 1911) *	217.96	305.89
Waidner and Burgess (1910)	217.98	306.02

* S.B.P. = 444.51 C. at constant volume.

SCALE OF RESISTANCE THERMOMETER (*Continued*)

	Freezing Points.			
	Sn	Cd	Pb	Zn
Callendar and Griffiths (1891)	231.9	320.8	327.8	419.0
Heycock and Neville (1897)	231.9	.....	.....	419.4
Waidner and Burgess (1909)	231.9	321.0	327.4	419.4
Holborn and Henning (1911)†	231.8_3	320.9_2	.....	419.4_0

	Freezing Points.				
	Sb	Al	Ag	Au	Cu
Heycock and Neville	630.0	656*	961.9	1063.5	1082
Waidner and Burgess	630.7	658	960.9	.....	1083

* Containing 0.5 per cent impurities. † S.B.P. = 444.5_1 C. at constant volume.

Use as a Standard. — In 1899, Callendar, at a meeting of the British Association for the Advancement of Science, in view of the relative ease and great precision of resistance measurements and the great difficulties in the use of the gas thermometer, suggested that the platinum thermometer be adopted as a secondary standard, reducing its readings as above indicated, and assuming as calibration points, 0°, 100°, 444.5°, the last being the sulphur boiling point on the constant-pressure scale. All platinum thermometers could then be compared with one selected as standard and calibrated as above indicated. He also pointed out that as regards portability and ease of reproduction, it is sufficient to send a few grams of the standard wire in an ordinary letter, to reproduce the scale with the utmost accuracy in any part of the world.

The work done in platinum and gas thermometry since 1899 abundantly justifies Callendar's suggestion of using the platinum thermometer as a secondary standard, since, as has been shown in preceding paragraphs, a resistance thermometer of pure platinum calibrated at three temperatures reproduces the gas scale with the greatest exactness to as high temperatures as the platinum thermometer can be used conveniently. It is not necessary, however, to compare a platinum thermometer with another taken as standard, if means are at hand for an independent calibration, since the characteristic constants of pure platinum are now known, and this metal can easily be had of sufficient purity to satisfy them. It is perhaps better to take the sulphur boiling temperature on the constant-volume scale, as most of the recent work in the determination of fixed points has been in terms of this scale.

For a platinum-resistance thermometer to serve as a secondary standard, therefore, provided its construction and use are otherwise correct, it is necessary and sufficient that its value of $\delta = 1.50$ (or 1.49 according to Holborn and Henning's scale) and of $C = 0.0039$, when calibrated in ice, steam, and sulphur vapor. (See chapter on Standardization.)

Sources of Error in Accurate Work. — *Heating by the Measuring Current.* — It is evident that if a too large current is sent through an electrical resistance thermometer, the heating thus occasioned will cause the indicated temperatures to be high. The limiting value of the current Callendar has shown to be about 0.01 ampere per 0.01 degree with an average platinum thermometer of wire 0.15 mm. in diameter. If a galvanometer of sufficient sensibility is used this effect is negligible, and when a greater current has to be used on account of lack of galvanometer sensibility, the heating effect may be maintained nearly constant by keeping the current constant by means of a rheostat in the battery circuit, since the resistance of the thermometer increases very nearly as fast as the rate of cooling, or a little faster than the temperature. Callendar also indicates that the heating effect is readily measured by using as current source two storage cells, connected first in parallel and then in series, the current heating correction being given by subtracting from the first reading one-third of the difference between the two readings.

Waidner and Burgess have also studied the heating effect of the measuring current and find that although this current may heat the coil to more than 1° C. above its surroundings, the value of the fundamental interval of the thermometer remains the same as when a current one-fifth as great is used.

The effect of using different measuring currents with a thermometer of $R_0 = 3.48\ \omega$ is shown below:

HEATING EFFECT OF MEASURING CURRENT.

Amperes.	R_0	F.I.	$R_{444.33}$	$pt_{S.B.P.}$	δ
$2.5 \cdot 10^{-3}$	3.48160	1.34115	9.13220	421.33	1.503
$10.0 \cdot 10^{-3}$	3.48174	1.34113	9.13213	421.31	1.505
$50.0 \cdot 10^{-3}$	3.48705	1.34114	9.13608	421.21	1.511
$100.0 \cdot 10^{-3}$	3.50373	1.34173	9.14832	420.69	1.545

HEATING OF PT COIL ABOVE SURROUNDING TEMPERATURE.

Amperes.	ΔT_0	ΔT_{100}	$\Delta T_{S.B.P.}$
$2.5 \cdot 10^{-3}$	0.001°	0.001°	....
$10.0 \cdot 10^{-3}$	.011	.010	....
$50.0 \cdot 10^{-3}$	.41	.41	.29
$100.0 \cdot 10^{-3}$	1.65	1.69	1.20

For a given small excess in temperature of the platinum coil above the temperature of its surroundings, the energy radiated in steam is 3.7 and in sulphur 52 times that radiated at 0° C., assuming that the radiation from platinum is proportional to the fifth power of the absolute temperature. For constant measuring current, the energy supplied to the coil at the S.B.P. is only 2.6 times the energy supplied at 0° C. It follows that the greater part of the energy loss is by convection and conduction rather than by radiation.

Lag of the Platinum Thermometer. — Inclosed as it necessarily is for most work in a sheath of porcelain, and possessing besides considerable mass, the platinum thermometer does not immediately assume the temperature of its surroundings. Put into a sulphur bath, it assumes an equilibrium condition in ten minutes. For small changes of temperature this effect is hardly perceptible and may be neglected in most practical work.

Inclosed in a thin flat-sided metal case (see Fig. 66), the temperature lag is practically nothing.

Insulation. — Defective insulation due to moisture condensed in the tubes is sometimes a source of error in accurate work at the ice point and lower temperatures with thermometers of high resistance if the tubes are not sealed. This may be readily done, if the containing sheath is of glass, by sealing the platinum leads into the glass so that they terminate in cups. When the containing sheath is of porcelain, as for high-temperature work, this sealing is not necessary, nor is it convenient; but running the leads into metal cups containing a fusible alloy still offers the readiest method of securing a good contact with the rest of the circuit.

Compensation for Resistance of the Leads. — It is necessary, in order to avoid thermal currents at the junctions with the thermometer proper and also evaporation and consequent change of resistance, to employ platinum leads from the thermometer to a point in the circuit at a constant temperature. Even if these leads are of relatively large diameter, there will still remain an error due to the varying resistance of these leads with change in temperature and with varying depth of immersion. It becomes necessary either to apply a "stem correction," which is troublesome and uncertain, or compensate for this effect as described under methods of measurement. Nowadays most platinum thermometers sold for industrial and scientific purposes are compensated. Uncompensated thermometers with gold leads are also to be found. They are not to be recommended for work of high accuracy. Silver leads are to be avoided.

The copper leads from the thermometer head to the measuring apparatus may be of appreciable resistance, and to render them flexible they are often stranded, when their resistance may vary somewhat. Thus Mr. F. W. Smith has found copper leads of $\frac{1}{40}\ \omega$ resistance to vary 1 or 2 per cent, giving 0.003° C. uncertainty at 0° C. In work of high accuracy it is evidently as important to keep the copper leads as constant as the platinum. It is now possible to obtain stranded wire in which each strand is enameled, and so eliminate the slip resistance.

In addition to the potential lead method, there have been bridge methods devised for the complete experimental elimination of all leads to the thermometer which is required in work of the highest accuracy, as it is extremely difficult, if not impossible, to make the compensation absolutely exact by adjustment in construction. These methods require, for the most part, rather elaborate experimental arrangements, for descriptions of which the reader is referred to the papers of Edwards,

W. Jaeger, and F. W. Smith. In brief, such methods depend either upon devices for alternately throwing the thermometer leads in the two sides of the bridge, measuring these leads, or eliminating them by use of the Kelvin double bridge or some modification.

Conduction along the Leads. — The thermometer leads may be the seat of another source of error, which increases in importance with the diameter of the leads, their length immersed, and the temperature gradient, namely, the effect of heat conduction along the leads influencing the resistance of the thermometer coil. This effect is especially to be looked for in four-lead bridge thermometers, where all four leads are of relatively heavy platinum. The best way to eliminate this source of error is to so design the instrument that it is negligible. Its presence may be recognized and corrected for by varying the depth of immersion of the thermometer in a bath at constant temperature.

Use of Impure Platinum. — The value of the constant δ in the Callendar formula (2), page 201, is a measure of the purity of the metal. For the purest platinum the value of δ is 1.500, assuming the S.B.P. = 444.70, and for impure platinum the value of δ increases with the impurity. Heycock and Neville made a study of the effect on the temperature scale obtained by using platinum of different degrees of purity, and concluded, erroneously it now appears, due to an incorrect method of calculation, that thermometers having different values of δ would give the same temperature scale when reduced by the parabolic formula of Callendar.

It has been shown since that impure platinum does not obey the same resistance-temperature law as the pure metal, and Waidner and Burgess have indicated the corrections to be applied to temperatures obtained by the Callendar method, using impure platinum to reduce to the usual temperature scale. They find, for platinum of varying degrees of purity as indicated by the values of δ, the following values for fixed points, using the Callendar equation in all cases for computing the temperatures:

FREEZING POINTS FOR VALUES OF δ INDICATED BELOW.

$\delta =$	1.505	1.570	1.803
Tin	231.90	231.82	......
Zinc	419.37	419.32	......
Antimony	630.70	631.25	632.65
Ag_3-Cu_2	779.2	......	784.6
Silver	960.9	966.2	975.3
Copper	1083.0	1092.0	1106.0

In Table VIII of the Appendix are indicated the corrections to be applied when using thermometers of impure platinum. Wires with a large δ are more liable to change with use, so that, although correct results may be obtained with them if properly reduced and checked up occasionally, it is preferable to use the purest platinum.

Changes in the Constants. — If platinum thermometers are repeatedly heated to temperatures in the neighborhood of 1000° C., or are kept for very considerable periods of time at even lower temperatures, changes in the value of the constants R_0, R_{100}, and δ will develop, necessitating frequent recalibration in work of high accuracy. Pyrometers for use at high temperatures should not be inclosed in inglazed porcelain even if the glaze does not touch the metal, as deterioration of the latter will otherwise ensue. The mica supports undergo distortion on cooling from high temperatures, increasing in size, tending to stretch the wire and increase its resistance. For this reason it is probably better to use the constants determined before a measurement at high temperature, rather than those determined afterwards. Again, if the wire of the thermometer has not been well annealed at a temperature higher than it is to be used, irregular changes will occur, which are the most marked for the first few heatings.

Waidner and Burgess find that for thermometers of pure platinum, the changes in their constants after the wires have been annealed are very much less than for those of impure platinum; thus, as shown in the accompanying table, which is typical, R_0 changes only by a few tenths of a degree for pure platinum, but by several degrees for impure. These changes are

CHANGES IN ZERO OF PLATINUM THERMOMETERS.

Thermometer of pure platinum.		Thermometer of impure platinum.	
$R_0=3.47971$ at start; $\delta=1.503$. $R_0=3.48164$ at end; diam. = .15 mm.		$R_0=21.3476$ at start; $\delta=1.570$. $R_0=21.0617$ at end; diam. = .10 mm.	
Changes in zero. °C.	History of thermometer previously annealed at 1200°.	Changes in zero. °C.	History of thermometer previously annealed at 1200°.
−0.005	After Zn F.P. 3 times.	−0.18	After Zn F.P. 10 times.
− .001	After Sb F.P. 1 time.	− .29	After Sb F.P. 7 times.
+ .007	After Sb F.P. 2 times.	−2.27	After 2 hrs. at 1100°+ C.
− .002	After 2 hrs. at 1100°+ C.	−3.94	After Cu F.P. 1 time.
− .050	After Cu F.P. 1 time.	−4.66	After Cu F.P. 1 time.
+ .013	After Cu F.P. 2 times.	−5.99	After Cu F.P. 2 times.
+ .138	After Cu F.P. 5 times.	−6.20	After Ag F.P. 2 times.
+ .144	After Ag − Cu F.P. 5 times.	−6.46	After Ag − Cu F.P. 4 times.

least for pure platinum wire of large diameter and suspended free from strains. For impure platinum wire, the effect of high temperatures is to decrease R_0 and to increase the fundamental coefficient, c; that is, the effect is as if the wire became purer, possibly because of the evaporation of impurities, for example, iridium. If the platinum is pure, the slight changes indicate a contamination of the wire and the effect of strains, as is evidenced by decrease in c and increase in R_0. The total change observed is the resultant of the effects of strains, of annealing, and of contamination and purification.

Use of Metals other than Platinum. — Holborn and Wien found that with palladium the absorption of hydrogen at low temperatures, giving the hydride, increases the resistance by 60 per cent; besides, the same effect of alteration as with platinum is noticed if the palladium is placed in hydrogen in the presence of silica. Palladium wound on mica and inclosed in porcelain has been shown by Waidner and Burgess to behave in a very similar manner as platinum to above 1000° C.; the law of the change of resistance of palladium with temperature is, however, very different from the Callendar equation, and is an equation of the fourth degree between 0° and 1100° C. for a precision better than 0.5° C., although up to 600° the Callendar equation is nearly satisfied.

No very definite conclusion is to be drawn from the work of Holborn and Wien with iridium and rhodium, except that these metals assume their normal resistance only after being heated several times to a high temperature. Iridium evaporates so much more readily than the others that it would seem the least best adapted for temperature measurement by means of the metals of this group, and platinum is evidently to be preferred.

Nickel is sometimes used in resistance thermometers, but it is not to be recommended for temperatures above 300° C., due to the change in the resistance-temperature relation as the transition temperature of nickel is approached and to oxidation at higher temperatures. Marvin has shown that for pure nickel the equation $\log R = a + mt$ holds approximately in the above limited range 0° to 300° C.

Conditions of Use. — The electrical resistance pyrometer of platinum seems, by reason of the great precision of the measurements which it allows, to be especially serviceable for laboratory investigations. It seems, on the other hand, to be too fragile for many of the industrial applications when there is rough handling, although it is very convenient in permanent installations when properly protected, and when it is desired to eliminate completely the often troublesome correction necessary for the temperature of the cold junction of the thermocouple.

The relation between the platinum-thermometer scale and the gas scale is well established to 1100° C., which is beyond the limit above which it is not safe to use the platinum-resistance pyrometer without frequent checking of its calibration.

The resistance pyrometer is the best instrument for differential work and for detecting small temperature changes as well as for controlling a constant temperature. It is also particularly adapted for use with recording instruments. Great care has to be taken that the platinum does not become contaminated.

Industrial Installations and Checking. — We have already called attention to the fragility of the fire end of a resistance thermometer and the necessity for protection of the coil from contact with furnace gases.

In industrial installations it is preferable to so mount the pyrometer that it may not readily be damaged by the furnace operations or by the handling of the pyrometer when necessary to withdraw it. This can usually be done by a suitable arrangement of the pyrometer within the furnace and by providing a convenient mechanism for withdrawing and holding the pyrometer free of the furnace. A design of bracket by Leeds and Northrup is shown for use with a small oil- or gas-burning furnace in Fig. 83. A sliding and slotted collar *L* carries the pyrometer on the arm *N*; the whole may be raised, caught, and turned on the pin *M*, permitting the removal of the pyrometer without shock and providing a resting place without

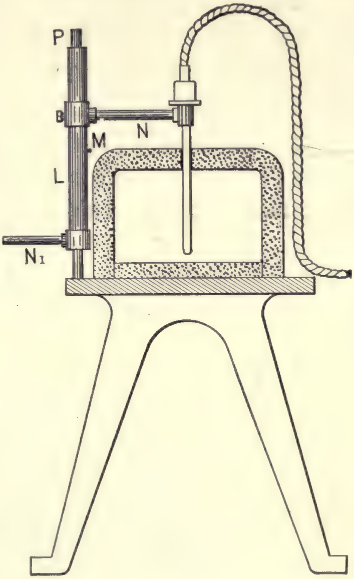


Fig. 83. Bracket Mounting.

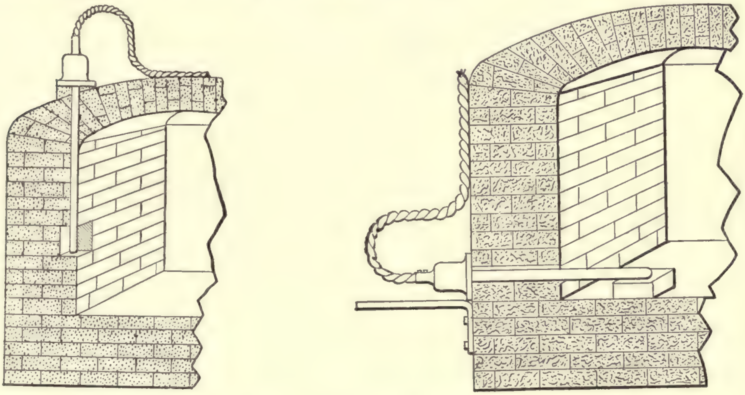


Fig. 84. Mountings in Oven.

handling or fear of breakage. Proper designs for mounting pyrometers in furnaces, kilns and duct pipes are shown in Figs. 83, 84, and 85. If the pyrometer tube be inserted horizontally supported only at one end, there is danger of bending and breaking even when the outer sheath is of metal.

The resistance pyrometer and its electrical circuit may be tested in place and the calibration verified without removal. An industrial installation should always be tested for proper insulation, not only when new but periodically, or when irregular behavior occurs. The actual operations of checking out the insulation, lead, and contact resistances will depend upon the design of the instrument and the voltage for which it is intended. It is safe to say that the resistance between any wire and the ground or thermometer case, or between two disconnected wires of the system, should be over 1 megohm per 100 volts.

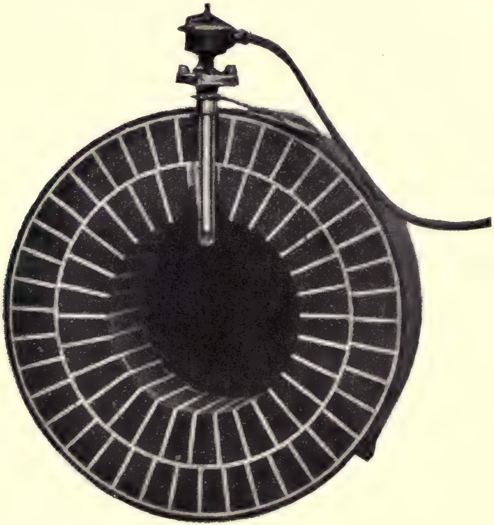


Fig. 85. Mounting in Duct.

Some of the manufacturers provide outfits for the automatic checking of thermometer indicators and coils. Thus, Leeds and Northrup furnish an equipment consisting of a series of coils corresponding to definite temperatures on the indicator, and another coil equal to the resistance of the thermometer at room temperature. The Cambridge Company also furnish " ice bobbins " by means of which the thermometer resistance may be checked at 0° C. The use of the resistance pyrometer industrially is also greatly facilitated by the practice that is becoming general among makers of constructing the instruments and all parts so that they are interchangeable. This is particularly necessary for multiple circuits using the same indicator or when using a single automatic recorder in connection with a number of indicators. These questions are considered in Chapter X.

CHAPTER VI.

THE LAWS OF RADIATION.

General Principles. — The temperature of bodies may be estimated from the radiant energy they send out, either in the form of visible light radiation or of the longer infra-red waves that are studied by their thermal effects. For the estimation of temperature in this way use is made of the laws of radiation.

Temperature and Intensity of Radiation. — When we consider the enormous increase in the intensity of radiation with rise in temperature, this method appears especially well adapted to the measurement of high temperatures. Thus, for example, if the intensity of the red light ($\lambda = 0.65\ \mu$) emitted by a body at 1000° C. is called 1, at 1500° C. the intensity will be over 130 times as great, and at 2000° C. over 2100 times as great.

The rapid increase of the photometric intensity of the light in comparison with that of the temperatures is shown by the following table, from Lummer and Kurlbaum, for light emitted by incandescent platinum. If I_1 and I_2 are the intensities of the total light emitted at the absolute temperatures T_1 and T_2 (not differing many degrees from one another), then if we write with Lummer and Pringsheim

$$\text{(A)} \qquad \frac{I_1}{I_2} = \left(\frac{T_1}{T_2}\right)^x.$$

the values of x at various absolute temperatures ($T°$ C. + 273°) are as follows:

$T°$ abs.	x.
900°	30
1000	25
1100	21
1200	19
1400	18
1600	15
1900	14

From this table it will at once be seen that at 1000° absolute (727° C.) the intensity of the light increases twenty-five times as rapidly as the temperature; at 1900° absolute (1627° C.) fourteen times as rapidly. The product $Tx = 25,000$ as shown by Rasch seems to express the relation between T and the exponent x.

Emissive Powers. — It would therefore appear that a system of optical pyrometry based on the intensity of the light emitted by incandescent bodies would be an ideal one, inasmuch as a comparatively rough measurement of the photometric intensity would measure the temperature quite accurately. This, however, is only partly true; it is limited somewhat by the fact that different bodies, although at the same temperature, emit vastly different amounts of light. Thus the intensity of the radiation from incandescent iron or carbon at 1000° C., for example, is many times greater than that emitted by such substances as magnesia, polished platinum, etc., at the same temperature. Consequently, if any conclusions were drawn as to the temperatures of these bodies from the light that they emit, it might lead to large errors. Thus at 1500° C. this difference in the intensity of the light emitted by carbon and by polished platinum would lead to a difference in the estimated temperature of these bodies of about 100° C., and less at lower temperatures.

The "Black Body." — Kirchhoff in one of the most important contributions to the theory of radiation was led to the important conception of what he termed a "black body," which he defined as one which would absorb all radiations falling on it, and would neither reflect nor transmit any. He further pointed out clearly the important fact that the radiation from such a black body was a function of the temperature alone, and was identical with the radiation inside an inclosure all parts of which have the same temperature. Various expressions are in use for the "black body," such as "integral radiator," "full radiator," etc.

Experimental Realization. — The first experimental realization of a black body as a practical laboratory apparatus was made by Lummer and Wien, by heating the walls of a hollow opaque inclosure as uniformly as possible and observing the radiation coming from the inside through a very small opening in the walls of the inclosure. No substance is known, however, whose surface radiation is exactly that of a black body. The radiations from such substances as carbon and iron oxide approximate fairly near to black-body radiation, while such bodies as polished platinum and magnesia, etc., depart very far from it. Black-body radiations, corresponding to temperatures from that of liquid air or lower, up to 2500° C. or higher (if suitable materials are chosen), are now available in the laboratory. For temperatures up to 600° or thereabouts, this is realized by immersing a metallic or other vessel in a constant-temperature bath (liquid, gas, vapor, or fused salt) and observing the radiation from the interior through a small opening in the walls. At higher temperatures it is very difficult to heat the walls of the inclosure uniformly, especially with gas flames. Lummer and Kurlbaum have very satisfactorily overcome this difficulty in their electrically heated black body, which is shown in section in Fig. 86.

The central porcelain tube is wound over with thin platinum foil through which an electric current is sent which can be adjusted to maintain any desired temperature up to 1500° C. This tube is provided with a number of diaphragms to minimize the disturbing effects of air currents. To protect this inner tube from external influences and to diminish unnecessary heat losses, it is surrounded by several porcelain tubes and air spaces, as shown in the figure. The radiation from the uniformly heated region near the center, and which passes out through the end of the tube at *O*, is a very close approximation of the ideal black-body radiation of Kirchhoff. The temperature of this central region is measured by means of one or more carefully calibrated thermocouples. By adding supplementary heating coils at the ends the temperature distribution may be improved. Waidner and Burgess were able to obtain a constancy of 1° C. throughout the greater part of the length of such an apparatus. The calibration of optical and radiation pyrometers is carried out by means of such a black body. For higher temperatures special furnaces are used, which we shall describe later.

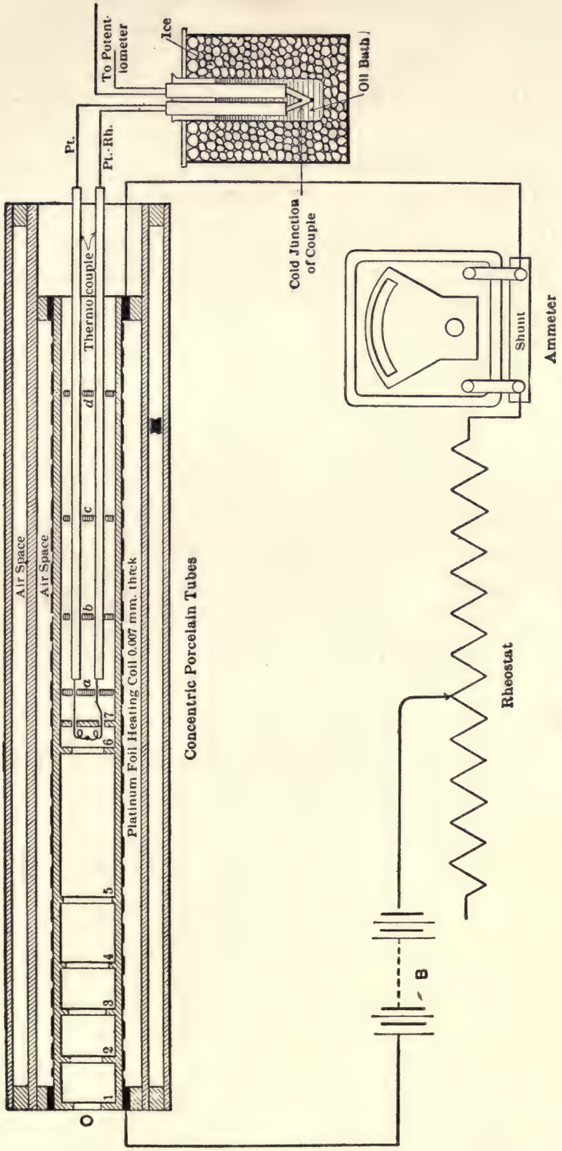


Fig. 86. Experimental Black Body.

As has already been stated, if magnesia, porcelain, platinum, iron, etc., are heated to the same temperature, they will emit vastly different amounts of light. If, however, these bodies* are heated inside a black body, they will all emit the same radiation, and on looking into the small opening all details of their contour will be lost, the whole region being of uniform brightness. Thus, in the black body described above, before the heating has become uniform, the platinum wires of the thermocouple can be seen as dark lines against the brighter background, but when the heating current has been maintained constant for some time, so that the heating has become uniform in the inner central chamber, the wires of the couple almost completely disappear, notwithstanding that, of all substances, platinum and the black oxide of the radiating walls differ most widely in their radiating powers (emissivities).

Realization in Practice. — Fortunately, in pyrometric practice it is often easy to realize very nearly the conditions of a black or totally absorbing body. Thus the interior of most furnaces, kilns, and ovens approximates this condition, or the bottom of a closed tube of any material thrust into any space heated to incandescence. Again, iron and coal observed in the open are not far removed in their optical properties from the black body.

Black-body Temperature. — The term "black-body temperature" has come into quite extensive use and is of great convenience in the discussion of pyrometric problems. The temperatures indicated by a radiation pyrometer that has been calibrated against a black body are known as black-body temperatures. Thus, were a piece of iron and a piece of porcelain both at 1200°, the optical pyrometer, which used the red light emitted by these bodies, would give, as the temperature of these bodies, 1140° and 1100° respectively. This means that iron and porcelain at 1200° emit red light of the same intensity as is emitted by a black body at 1140° and 1100° C. respectively. The "black-body temperature" of these materials for green light might differ quite appreciably from that for red light. It is at once evident that if the "black-body temperatures" of different bodies, e.g., carbon and platinum, are equal, their actual temperatures may differ considerably (180° C., or so, at 1500° C.). This violates our ordinary conception of equal temperatures, which is based on thermal equilibrium between the bodies if brought into contact. The term "equivalent temperature," suggested by Guillaume, is also used for "black-body temperature." Waidner and Burgess have suggested the notation: $1500° K_{.65}$, meaning 1500° absolute centigrade as viewed with light of wave length 0.65μ.

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* It is here assumed that the radiation is purely thermal and that no part is due to luminescence, as the laws of radiation are only directly applicable where such is the case.

The temperature of any body, therefore, as measured by an optical or by a radiation pyrometer, will always be lower than its true temperature by an amount depending on the departure of its radiation from that of a black body. There is another source of error, however, that may act in the direction of making the pyrometer read too high, due to light reflected by the body whose temperature is being measured. This source of error may very often be eliminated, where the accessibility of the work permits, by running a tube down to the incandescent surface, which will cut off stray radiation from the surrounding flames. The magnitude of the error that may arise from light reflected from surrounding hotter objects may be quite considerable (several hundred degrees), depending on the temperature, area, and position of the surrounding hot objects and the reflecting power of the surface whose temperature is under observation.

Kirchhoff's Law. — If we consider an opaque object and let radiation fall upon it, the relation between the proportions reflected (r) and absorbed (a) is:

$$r + a = 1.$$

For such objects, therefore, eliminating the effects of polarized light and angle of incidence and assuming we are dealing with matt surfaces and thermal radiation only, the determination of either the absorbing or reflecting power gives also the other.

The quantity a depends on the nature of the substance and is a function of the wave length and temperature only, or

$$a = f(\lambda, T).$$

For a radiating body the emissive power e is a similar function of λ and T.

By definition, a black body absorbs all the radiation incident upon it, therefore in this case $a = 1$ and $r = 0$ for all values of λ and T. The emissive power ϵ of a radiating black body is evidently fundamental to the theory of radiation, and the function $\epsilon = F(\lambda, T)$ forms the basis of several of the radiation laws.

Kirchhoff's law as applied to monochromatic radiation may be stated in the following way: $e = a\epsilon$, or more completely:

$$\frac{e}{a} = \ldots \frac{e_n}{a_n} = \epsilon \equiv F(\lambda, T).$$

The ratio of the emission to the absorption is for all bodies the same function of wave length and temperature, and is equal to the emission of a black body.

There are a number of corollaries to Kirchhoff's law, some of which we may emphasize as being of interest in temperature measurements, bearing in mind that we are here dealing only with radiation due to thermal causes.

The emissive power of a black body is greater than that of any other body at the same temperature. Every body absorbs the same rays that it emits at a given temperature. It may also absorb other rays, but they will be among those that a black body does not emit at the given temperature.

In general, the ratio $e:a$, which is the same for all bodies for given values of λ and T, does not depend on the degree or kind of polarization of the radiation.

The energy curves $e = f(\lambda)$ for each value of T lie wholly within the corresponding black-body curves $\epsilon = f(\lambda)$.

In the case of composite radiations, that is, of spectral bands having for limiting case the whole spectrum, Kirchhoff's law applies only under special conditions. Thus Kirchhoff's law holds for any composite radiations, taken between the limits λ_1 and

λ_2, if the total absorption is referred to the radiation from a black body at the same temperature as the bodies to be compared.

Again, Kirchhoff's law holds for composite radiations, when the two given bodies are at the same temperature and when each of them serves as source to the radiation which measures the total absorption of the other.

A corollary of considerable practical importance is the following: If two surfaces of any substances whatever at the same temperature radiate only on each other, the radiation from each is equivalent to the emission of a black body; from which it follows that, within an inclosed space at constant temperature, all bodies emit radiation identical to that of a black body. And finally, the radiation from a small opening in such an inclosure at constant temperature is black-body radiation, and depends only on the temperature.

It is worthy of remark that in the measurement of radiation from such a black body the receiver should also be a black body, or at least its coefficient of absorption should be known for the kind of radiation to be studied, if the radiation laws as applied to a black body are assumed to hold, as is often the case.

Stefan's Law. — Naturally the first numerical relation sought between intensity of radiation and temperature was one for the total energy of radiation sent out by a body, as it required less delicate instruments for measurement than the study of the spectral distribution of energy. Numerous attempts to express such a relation were made by Newton, Dulong and Petit, Rosetti, and others. These attempts, however, merely resulted in empirical expressions that held only through narrow ranges of temperature. The first important step was made by Stefan, who examined some of the experimental data of Tyndall on the radiation of incandescent platinum wire in the interval 525° C. to 1200° C., and was led to the conclusion that the energy radiated was proportional to the fourth power of the absolute temperatures. This relation seemed to be further supported by the best experimental data of other observers, at least to within the limit of accuracy of their observations, being strictly true, however, only for the energy of total radiation from a black body. This relation received independent confirmation from Boltzmann, who deduced it from thermodynamic reasoning. The conditions imposed by Boltzmann in his discussion on the nature of the radiation were such as are fulfilled by the radiation from a black body. This relation, which has now come to be generally known as the *Stefan-Boltzmann radiation law,* may then be stated as follows:

The total energy radiated by a black body is proportional to the fourth power of the absolute temperature, or

$$\text{(B)} \qquad E = \sigma\,(T^4 - T_0^{\,4}) = \int_0^\infty \epsilon\,(\lambda,T)\,d\lambda,$$

when E is the total energy radiated by the body at absolute temperature T° to the body at absolute temperature T_0°, and σ is a constant depending on the units used. Usually T_0 is small compared with T, so that practically we may write

$$\text{(B}'\text{)} \qquad E = \sigma T^4.$$

This law has received abundant experimental support from the researches of Lummer, Kurlbaum, Pringsheim, Paschen, and others, throughout the widest range within which temperature measurements can be made.

An illustration of the experimental evidence in support of this law is given in the table taken from the experiments of Lummer and Kurlbaum.

Absolute temperature.		$\sigma = \dfrac{E}{T^4 - T_0^{\,4}}$.		
T	T_0	Black body.	Polished platinum.	Iron oxide.
372.8	290.5	108.9	.....	....
492	290	109.0	2.28	33.1
654	290	108.4	6.56	33.1
795	290	109.9	8.14	36.6
1108	290	109.0	12.18	46.9
1481	290	110.7	16.69	65.3
1761	290	.....	19.64	.....

It will also be seen from this table that while the intensity of the total radiation of iron oxide is 4 or 5 times that of polished platinum, it is still considerably less than that emitted by a black body. The total radiation from objects other than a black body increases more rapidly than the fourth power of the absolute temperature, so that as the temperature is raised the radiation of all bodies appears to approach that of the black body. Whether or not there is a maximum limiting value of radiation due to purely thermal causes, is still an unsettled question, however.

The numerical value of the constant σ for a black body is of interest in absolute measurements and in checking the constants of radiation instruments. For the radiation per degree C. from 1 $\overline{\text{cm.}}^2$, expressed in gram-calories per second, the values found for σ range from less than $1.0 \cdot 10^{-12}$ by Bottomly and King to $1.52 \cdot 10^{-12}$ by Féry. The following observers, however, have obtained results agreeing more closely:

Kurlbaum,	$1.277 \cdot 10^{-12}$
Valentiner,	1.286
Bauer and Moulin,	1.275

$$\text{Mean} = 1.279 \cdot 10^{-12} \approx 5.34 \cdot 10^{-12} \frac{\text{watts}}{\overline{\text{cm.}}^2}.$$

The last two series of measurements were carried out over very extended temperature intervals — in the case of Valentiner to nearly 1600° C. His results correspond to the temperature scale, established by Holborn and Valentiner. It should be noted, however, that if compensating errors are present in the energy measurements or in the non-blackness of the radiator or receiver, it is possible to obtain a correct value of σ from an incorrect temperature scale, as is evident from the logarithmic form of the Stefan-Boltzmann equation: $\log E = \log \sigma + n \log T$.

Laws of Energy Distribution. — Among the first facts to be noticed about the nature of the radiations sent out by bodies were, that at low temperatures these radiations consisted of waves too long to affect the human eye. As the temperature was raised, shorter and shorter waves were added, which could finally be detected by the eye; the first of the visible radiations producing the sensation called red, then orange, etc., until the violet waves were reached, which were the shortest waves that the eye could detect.

Soon after Langley brought out the bolometer, which was so admirably adapted to the measurement of the minute energy of radiations, a great mass of valuable experimental data was obtained, bearing on the spectral distribution of the energy of the radiation emitted by various bodies. Among the most important of these contributions must be mentioned the researches of Paschen, who examined the distribution of energy in the emission and absorption spectra of various substances. Among the experimental facts established by these researches were, that by far the largest portion of the energy in the spectrum was found in the infra-red region, that the position of the wave length having the maximum energy depended on the temperature of the body, and that, as the temperature was raised, the energy of all the waves emitted increased, but the shorter waves more rapidly than the longer, so that the position (wave length) of maximum energy in the spectrum shifted toward shorter wave lengths. These facts are well illustrated by the curves shown in Fig. 85, taken from a paper by Lummer and Pringsheim, in which the ordinates are proportional to the intensity of radiation emitted by a black body, and the abscissas are wave lengths (in thousandths of a millimeter). Such curves, as are here shown, where the temperature is constant and the energy is measured corresponding to radiations of different wave lengths emitted by a body, are called *energy curves*, i.e., the relation determined is $I = f(\lambda)$ for T = constant, where I = energy corresponding to wave length λ, strictly the energy comprised in the region of the spectrum between λ and $\lambda + d\lambda$, and T is the absolute temperature of the radiating source. It is also interesting to study the change in the intensity of some particular wave length as the temperature of the radiating source is changed, i.e., to find $I = F(T)$ for λ = constant. This can of course be done by exposing the bolometer strip in a fixed part of the spectrum and observing the galvanometer deflections as the temperature is changed. The curves obtained in this way for $I = F(T)$ are called *isochromatic curves.*

Wien's Laws. — Wien was led from theoretical considerations to state that "when the temperature increases, the wave length of every monochromatic radiation diminishes in such a way that the product of the temperature and the wave length is a constant,"

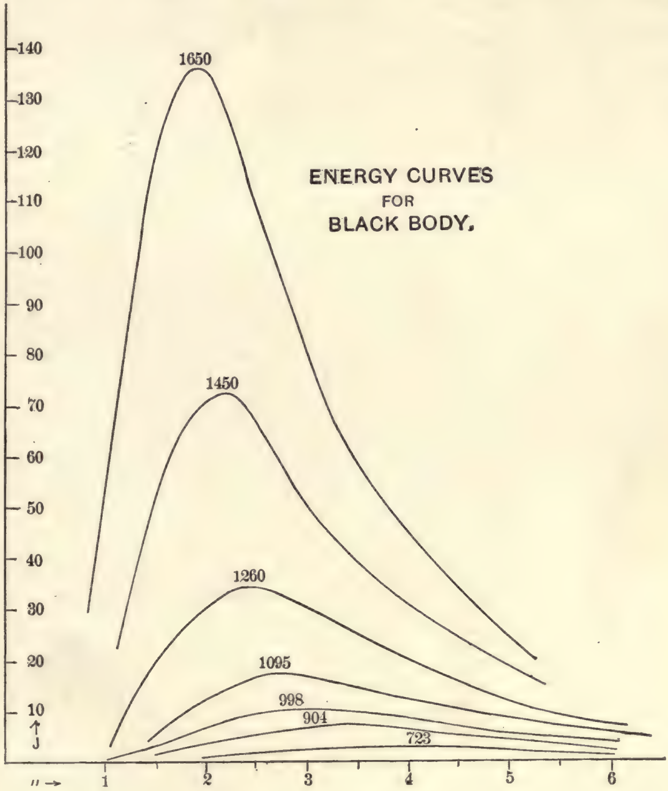

Fig. 87. Energy Curves.

$$\lambda T = \lambda_0 T_0.$$

Hence for the wave length of the maximum energy, λ_m, we have

$$\lambda_m T = \text{const.} \quad \dots\dots\dots \quad (I)$$

This is known as the "Wien displacement law" and is simply a mathematical statement of the fact that as the temperature of the radiating source is changed the wave length having maximum energy in the spectrum will be changed in such a way that the product of this wave length and the corresponding absolute temperature of the source, T, is equal to a constant. Wien then combined the above relation with the Stefan-Boltzmann law and was led to the relation that

$$I_{\text{max.}}\, T^{-5} = \text{const.} = B, \quad . \quad . \quad . \quad . \quad . \quad (\text{II})$$

in which $I_{\text{max.}}$ indicates the energy corresponding to the wave length of the maximum energy and T is the absolute temperature of the radiating source (black body). Both of these generalizations of Wien for the radiations emitted by a black body have received the most convincing experimental verification throughout the widest ranges of measurable temperatures that are at present available to the experimentalist.

As an illustration of the experimental evidence in support of these two laws of radiation, the following table has been added, taken from a paper by Lummer and Pringsheim on the radiation from a black body:

λ_m	I_m	$A = \lambda_m T$	$B = I_m T^{-5}$	Absolute temperature.	$T = \sqrt[5]{\frac{I_m}{B_{\text{mean}}}}$	Diff.
4.53	2.026	2814	2190.10^{-17}	621.2°	621.3	+0.1°
4.08	4.28	2950	2166	723.0	721.5	−1.5
3.28	13.66	2980	2208	908.5	910.1	+1.6
2.96	21.50	2956	2166	998.5	996.5	−2.0
2.71	34.0	2966	2164	1094.5	1092.3	−2.2
2.35	68.8	2959	2176	1259.0	1257.5	−1.5
2.04	145.0	2979	2184	1460.4	1460.0	−0.4
1.78	270.8	2928	2246	1646.0	1653.5	+7.5
Mean.........		2940	2188.10^{-17}			

As will be seen, these results of experiment are in most satisfactory agreement with these laws, when one considers the experimental difficulties that are involved in the measurements. In the value for B the temperature enters to the fifth power, so that a small error in the temperature produces a very marked effect on the value of B. Paschen later obtained $\lambda_m T = 2920$.

Wien also published the result of a further theoretical investigation on the spectral distribution of energy in the radiation of a black body, in which he was led to the conclusion that the energy I corresponding to any wave length was represented by

$$I = c_1\lambda^{-5}\epsilon^{-\frac{c_2}{\lambda T}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(III)}$$

where I is the energy corresponding to wave length λ, T is the absolute temperature of the radiating black body, ϵ is the base of the natural system of logarithms, and c_1 and c_2 are constants. We have further the relation: $c_2 = 5\,\lambda_m T$, to which we may assign the value $c_2 = 14{,}500$.

The subsequent experimental work of Beckman, Rubens, and others has shown that Wien's distribution law does not hold for long wave lengths, although it amply suffices throughout the whole visible spectrum, and may be applied in all cases where $\lambda T < 3000$.

Planck has deduced an expression analogous to Wien's which applies with exactness for all wave lengths and temperatures. His law, which reduces to Wien's for small values of λ, may be written

$$I = c_1\lambda^{-5}\left(\epsilon^{\frac{c_2}{\lambda T}} - 1\right)^{-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(IV)}$$

in which $c_2 = 4.965\,\lambda_m T$, a more exact solution than that given by Wien's law III.

Other radiation laws have also been suggested, but Planck's seems to best satisfy both experiment and theory.

For the radiation from all substances that have been examined experimentally, it has been found generally that the "displacement law,"

$$\lambda_{m_1} T = \text{const.} = A_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(Ia)}$$

still holds true, although the radiation may depart far from that for a black body. In this case, however, the value of the constant is different from that for a black body. Thus for polished platinum Lummer and Pringsheim found $A_1 = 2626$.

For the radiation from other than a black body the law of maximum energy applies only in the modified form

$$I_m T^{-\alpha} = \text{const.} = B_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(IIa)}$$

where α cannot be less than 5 and is not probably ever greater than 6, the value found by Lummer and Pringsheim for polished platinum. The general form of Wien's law (III) takes the form

$$I = c_1 \lambda^{-\alpha} \epsilon^{-\frac{c_2}{\lambda T}}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(III}'\text{)}$$

where $6 > \alpha > 5$.

The corresponding form assumed by Stefan's law for non-black bodies is

$$E = \sigma' T^{\alpha - 1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(B}'\text{)}$$

where α is the same as in the preceding equation.

Lummer and Pringsheim found the following limits of temperature as given by the Wien relation (Ia):

	λ_m	$T_{\text{max.}}$	$T_{\text{min.}}$
Electric arc	0.7μ	4200 abs.	3750 abs.
Nernst lamp	1.2	2450	2200
Auer burner	1.2	2450	2200
Incandescent lamp	1.4	2100	1875
Candle	1.5	1960	1750
Argand burner	1.55	1900	1700

Lummer and Pringsheim also heated a carbon tube electrically to about 2000° C. and observed the temperature inside simultaneously with instruments making use of the several radiation laws:

Method.	T absolute.
Photometric	2310 2320 2330
Total radiation	2330 2345 2325
Energy maximum	2330 2320

This complete concordance at such a high temperature between the different radiation methods gives further confidence in the legitimacy of their indefinite extrapolation for nonluminescent bodies. Waidner and Burgess have also found that this accord probably exists at the temperature of the electric arc, 3600° C.

In spite of the excellent agreement among the above-mentioned experiments in confirming the validity for temperature measurements of the several radiation laws, there is, nevertheless, too great an outstanding uncertainty in the numerical values of the characteristic constants of the equations representing these laws, such, for instance, as the σ in Stefan's law (B), page 246, and the c_2 in the Wien equation (III), page 251, for black-body radiation, as well as in the corresponding quantities, and particularly the value of the exponent α (equation (II), etc.), for other substances.

We have seen (page 80) that there is a discrepancy of considerable magnitude, of at least 25° C., at the melting point of palladium, on the scale of the nitrogen-gas thermometer as given by Holborn and Valentiner and by Day and Sosman. The measurements of the former, made simultaneously with the gas-thermometer determinations, lead to a value of $c_2 = 14{,}200$ in Wien's equation (III), and in the hands of Valentiner to a constant value of 5.34 watts for σ in Stefan's equation (B). The gas scale of Day and Sosman, however, corresponds more nearly to a value of $c_2 = 14{,}500$ as deduced from the optical measurements of Nernst and Wartenberg and of Waidner and Burgess. It is very important that this outstanding discrepancy be settled, and further work is in progress in several laboratories on these and allied subjects.

Warburg and Leithauser, in a preliminary announcement of new determinations of c_2 made at the Reichsanstalt, find values ranging between 14,200 and 14,600, depending on the experimental conditions. Their best value so far announced is 14,570.

Coblentz at the Bureau of Standards has also published preliminary results on c_2 approximating 14,600.

Applications to Pyrometry. — It is evident that theoretically any of these laws and their various consequences might be used as a basis of pyrometry, but practically it is not convenient to make use of all of them. The displacement law ($\lambda_m T = A$) and the maximum-energy law ($I_m T^{-5} = B$) of Wien are well-established relations, but in practice it is exceedingly difficult to construct instruments of sufficient sensibility to give any considerable precision, and any industrial pyrometer using these principles is out of the question at the present time. The reason of the lack of sensibility with the relation $\lambda_m T = A$ is due to the fact that the exact position of the wave length possessing the maximum of energy is very difficult to locate, especially at relatively low temperatures (see Fig. 87). The value of the maximum energy could perhaps be measured more readily, but as this quantity varies as the fifth power of the temperature, there would hardly be any preference for this over the former method.

There have been, however, several most convenient, simple, and very accurate instruments devised which are based either on the use of Stefan's law, $E = \sigma\,(T^4 - T_0^4)$, or Wien's distribution law, $I = c_1\lambda^{-5}\epsilon^{-\frac{c_2}{\lambda T}}$, either directly or indirectly, and in the two following chapters we shall treat of these at some length.

The last equation is conveniently put into the logarithmic form for computation:

$$\log I = C - \frac{c_2 \log \epsilon}{\lambda} \cdot \frac{1}{T},$$

or, when comparing two intensities, as in temperature measurements, the determination of an absorption or reflection coefficient, or when comparing one type of radiation with another, we have:

$$\log \frac{I}{I_1} = \frac{c_2 \log \epsilon}{\lambda}\left(\frac{1}{T_1} - \frac{1}{T}\right) \cdot \quad . \quad . \quad . \quad . \qquad \text{(IIIa)}$$

By expressing numerical results graphically, it is evident that $\log I$ *vs* $\frac{1}{T}$ is a straight line, which greatly simplifies the reduction of observations. It will be seen also that the constant c_2 must be known exactly if (IIIa) is to be used as a basis of correct temperature measurement. Unfortunately there is still a considerable lack of certainty in our knowledge of this constant, as shown above, although its value has been shown by several observers to remain sufficiently constant throughout the visible spectrum. We shall use the value $c_2 = 14{,}500$ in what follows.

It has been shown by Henning, v. Wartenberg, and others that the absorption coefficient a, for the various wave lengths of the visible spectrum, does not change appreciably with temperature, at least for several of the metals; and this fact may be taken advantage of in temperature measurements when sighting on an object for which we know the value of the absorption coefficient a, the reflection coefficient $r = 1 - a$, or the emissivity $e = a$ when that of a black body is taken as unity. If S_λ is the black-body temperature absolute $(= s + 273)$, that is, the apparent temperature of the substance as given by an optical pyrometer, using light of wave length λ, and T $(= t + 273)$ the corresponding true temperature of the substance, then Wien's equation gives:

$$\frac{1}{T} - \frac{1}{S_\lambda} = \frac{\lambda}{c_2 \log \epsilon} \cdot \log a. \quad . \quad . \quad . \quad . \qquad \text{(IIIb)}$$

This form of Wien's equation is of the greatest importance in the practical application of optical pyrometry to the estimation of the temperature of incandescent metals and other substances for which the absorption coefficients are known.

It is also possible to estimate a temperature by Wien's law from the measurement of the light intensity at two wave lengths. The general expression is:

$$\log \frac{I_1}{I_2} = 5 \log \frac{\lambda_2}{\lambda_1} + \frac{c_2 \log \epsilon}{T}\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right) + \log \frac{a_1}{a_2} \quad . \quad . \qquad \text{(V)}$$

where a_1 and a_2 are the absorption coefficients for the wave lengths λ_1 and λ_2, and where I_1 and I_2 are the corresponding intensities corrected for the sensibility of the eye. In the case of a black body, the last term is zero. The eye-sensibility correction is different for each individual and the visibility curve usually has the general form shown in Fig. 88 as given by Nutting for several observers and reduced to a common maximum.

In view of their general utility in the application of optical pyrometers to the measurement of the temperatures of exposed surfaces, we give in the Appendix, Table X, the values of the emissivities or absorption coefficients ($a = e/\epsilon$), where $\epsilon = 1$, for certain opaque substances as determined by various observers; and if the assumption is made in all cases that a has no, or a very small, temperature coefficient, the above equations may be used to compute the true temperatures of such substances when their absorbing power a is known, as well as their apparent temperatures as given by an optical or radiation pyrometer, remembering that the above formulæ apply only when expressed in degrees absolute ($t + 273°$ C.).

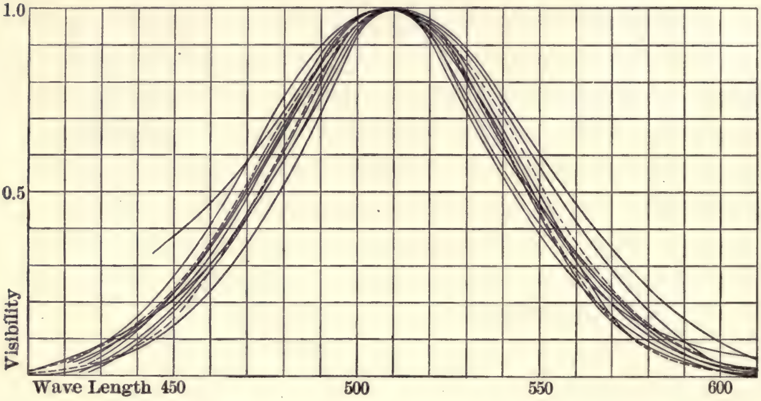

Fig. 88. Visibility Curve of Eye.

We may illustrate by a numerical example the use of Table X for the estimation of the true temperature of a metal from observations with an optical pyrometer, using red light of wave length $\lambda = 0.65\ \mu$. Let us take the case of the pouring of a stream of *iron* whose surface is clear, and suppose the optical pyrometer reading to be 1427° C. when the pyrometer is sighted on the clear stream. From Table X, the value of the absorption coefficient a for iron at $\lambda = 0.65\ \mu$ is 0.415. In equation (IIIb), we have to solve for T as follows:

$$\frac{1}{T} - \frac{1}{1427 + 273} = \frac{0.65 \cdot \log 0.415}{14{,}500 \cdot 0.4343},$$

whence $t = T - 273 = 1549°$ C., the true temperature of the stream of metal.

Equation (IIIb) may also be solved graphically as shown in Fig. 89, for pyrometers using red light, in which each of the curves represents a given absorbing, emissive, or reflecting power $(a = e = 1 - r)$, the abscissæ are pyrometer readings in centigrade, and the ordinates the corresponding corrections to be added to the pyrometer readings for substances of known emissive powers. Similar graphs could be constructed for pyrometers using other than red light. Methods of graphical reduction have

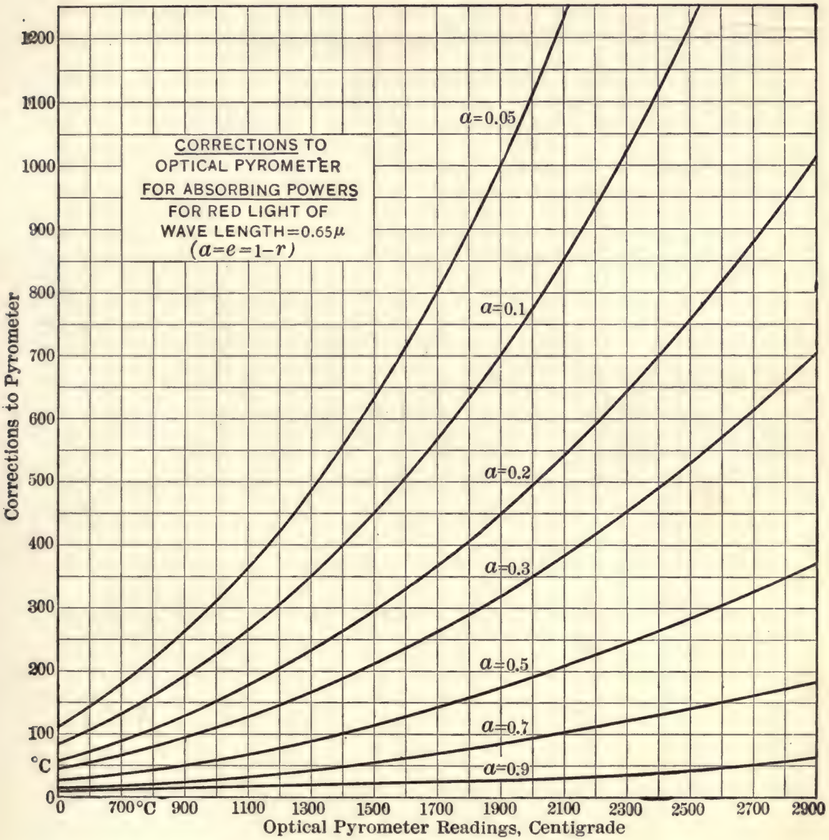

Fig. 89. Corrections to Optical Pyrometer.

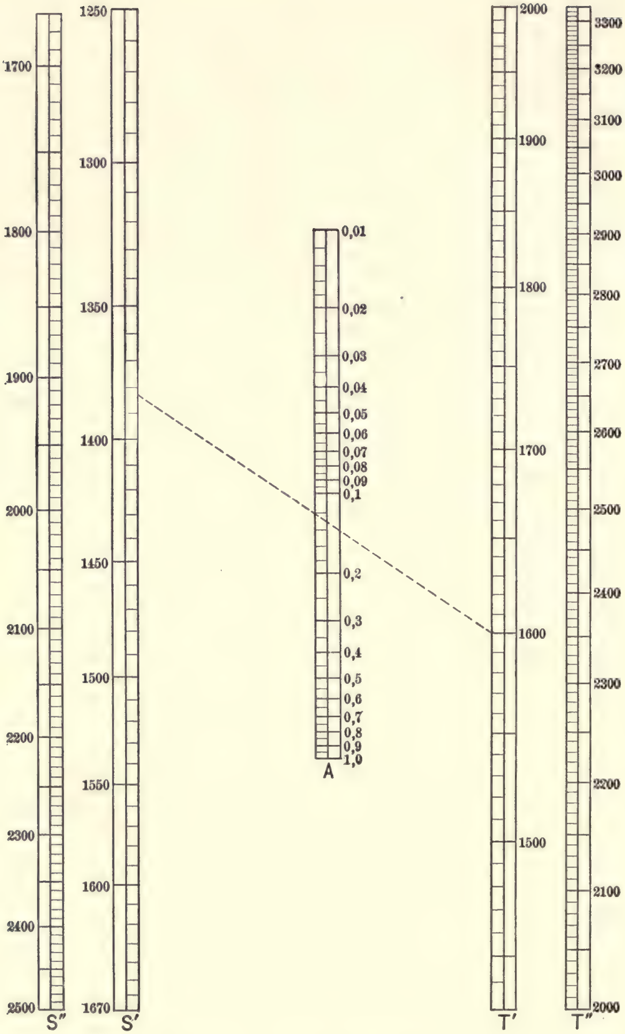

Fig. 90. Pirani's Method.

also been described by Wartenberg, who plots lines of temperature readings with absorption coefficients as ordinates and temperature corrections as abscissæ; and by Pirani, who has devised a protractor or vernier method for the solution of Wien's equation, reproduced in Fig. 90, in which a line drawn from any observed temperature S or S_1 through the value a of the absorption coefficient for the substance observed intersects the lines T or T_1 at the point corresponding to the true temperature. This figure is constructed for $\lambda = 0.65\ \mu$ and $c_2 = 14{,}200$. To transform the value of a to the basis of any other value of c_2, as 14,500, use may be made of the equation $\alpha \log a = \log a'$, where α is the ratio of the c's. (See also Table IX in the Appendix.)

It should be noted, in making use of the figures given in Table X, that they apply, with some exactness, in the case of the metals, to bright or polished surfaces only of either the solid or liquid. When rough surfaces are met with, the values of the absorbing factors should in general be increased considerably over those given in the table. Also, these last are uncertain for a single metal, in some cases by as much as 10 per cent, as determined by different observers, due in large part, apparently, to the varying degree of polish of the samples used. Also, it should be noted that the surfaces of many substances undergo changes of emissivity on continued heating.

The expression for the emissivity E_x of total radiation, to use with radiation pyrometers based on Stefan's law, is:

$$\log E_x = 4\,(\log T - \log S). \quad . \quad . \quad . \quad . \quad \text{(Ba)}$$

There is little data on the total emissivity E for either the metals or other substances of interest in the measurement of temperatures by means of total-radiation pyrometers. A rough idea of the order of the value of the total emissivity E (equation (Ba)) is given by an examination of both the visible and infra-red values of the absorbing powers. The values at 2, 5, and 8μ are given in Table X. Thus for iron, the average value of a from the table is 0.28, and the observed value of E is 0.29. The infra-red values of a as well as those of E, in general, vary with the temperature, which fact renders their exact determination for high temperatures a difficult operation. Determinations of E at high temperatures have been made for liquid copper, 0.14; iron, 0.29; cuprous oxide, 0.60.

There is room for a great deal of experimental work in determining satisfactorily the emissive properties at high temperatures of those substances met with in pyrometric practice.

CHAPTER VII.

RADIATION PYROMETER.

Principle. — The quantity of heat a body receives by radiation from another body depends on certain conditions relative to each of the two bodies, which are:

1. Temperature;
2. Area of surface;
3. Distance apart;
4. Emissive and absorbing power.

In order to utilize heat radiation for the determination of temperatures, one measures a heat change produced on the object used as an instrument by the object to be studied; this heat change is either a rise of temperature or a resulting phenomenon, such as a change of electrical resistance, thermoelectromotive force, expansion, etc.

The quantity of heat given off is proportional to the area of the radiating surface S, and varies inversely as the square of the distance l.

$$q = k\frac{S}{l^2} = k'\frac{d^2}{l^2} = k''E \cdot \frac{d^2}{l^2},$$

d being the diameter of the radiating surface and E its emissive power.

Now, $\frac{d}{l}$ is the apparent diameter of the object; the quantity of heat radiated depends, then, upon the solid angle under which the object is seen. Any instrument making use of the intensity of radiation must, therefore, have a receiving device of sufficiently small area so that it may be completely covered by the desired radiation.

The emissive power E is very variable from one substance to another, as we have seen, and for the same substance variable with the temperature. It would be desirable to determine this, but that is difficult and often impossible, especially at high temperatures, although some small advance has been made in this direction for a few substances, as we have seen in the preceding chapter.

The coefficient k'' is a function of the temperature alone, which expresses the law of variation of the radiation with the temperature. This law should be determined in the first place. It is on the more or less exact knowledge of this law that the entire accuracy of the results depends. We have seen that Stefan's law (page 245) satisfies all requirements, at least in the case of black bodies, for the measurement of total radiation, although the early experimenters, working before the establishment of this law, were obliged to express their results empirically, and great confusion resulted from the different assumptions made.

Early Investigators: Temperature of the Sun. — Let us see now what are the experimental arrangements which have been used to measure the intensity of heat radiation; these earlier measurements had for their only aim the determination of the sun's temperature.

Later were developed the more elaborate and sensitive types of apparatus which were suitable also for laboratory investigations, and which were used, for example, in the experimental demonstration of the laws of radiation; and finally we have to-day several total-radiation pyrometers of simple construction which are of great usefulness both as industrial and as scientific instruments.

We shall consider in order the above-mentioned aspects of this development of total-radiation methods, noting that the early observers labored under a threefold handicap,—lack of knowledge of the temperature scale, of the radiation laws, and lack of sufficiently sensitive instruments.

Pouillet's Pyrheliometer. — Before Pouillet, Gasparin had already made some trials. His apparatus consisted of a hollow brass sphere mounted on a foot and blackened; a thermometer was used to measure the rise in temperature of the water contained in the sphere. The advantage of this arrangement was that the apparatus was always turned properly toward the sun.

The pyrheliometer of Pouillet consists of a calorimeter which measures directly the heat received by radiation (Fig. 91). A very thin silver box is carried by a hollow tube, cut along a generatrix to let the thermometer be seen. The box is of 100 mm. diameter by 15 mm. height; it contains 100 c.c. of water. At the lower part of the box is located a metallic disk of the same diameter as the box, and serving to turn the apparatus toward the sun; it suffices, in fact, for the shadows of the box and disk to coincide exactly in order that the system be properly pointed. A knob serves to turn the apparatus about its axis in order to stir the water. Finally a support gives the means of placing the system in any desired orientation.

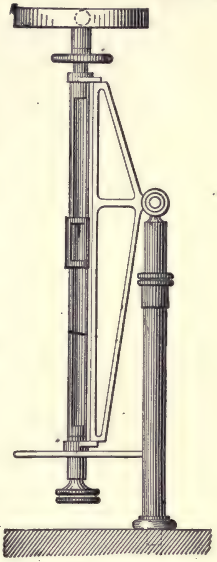

Fig. 91. Pouillet's Pyrheliometer.

To take an observation, the apparatus is set up and shielded from the sun's action by means of a screen; the readings of the thermometer are taken for five minutes; the screen is removed and the thermometer is read for five minutes; the screen is put back, and a new set of readings of the thermometer for five minutes is taken.

The first and the third sets furnish the corrections due to the surroundings. Pouillet observed in this way a rise of temperature of one degree in five minutes.

In the determination of the temperature of the sun, it was evidently necessary to take into account the heat absorbed by the atmosphere (it is about 20 per cent of the total radiation from the sun). Pouillet found by this method 1300° for the temperature of the sun.

Violle's Actinometer. — The principle of this apparatus is quite different from that of the preceding; one observes the stationary equilibrium of a thermometer receiving simultaneously radiation from an inclosure at fixed temperature, and that from the hot substance to be investigated (Fig. 92).

The apparatus consists of two spherical concentric coverings of brass, in which a water circulation may be set up at constant temperature, or ice may be substituted for water. The inner covering of 150 mm. diameter is blackened inside. The thermometer has a spherical bulb whose diameter varies from 5 to 15 mm.; the surface of the bulb is also blackened. The scale is divided into fifths of a degree. The entrance tube carries a diaphragm pierced with holes of different diameter; on the extension of this tube is located an opening closed by a ground-glass mirror slightly blackened, which permits of determining that the solar rays fall quite exactly upon the thermometer bulb.

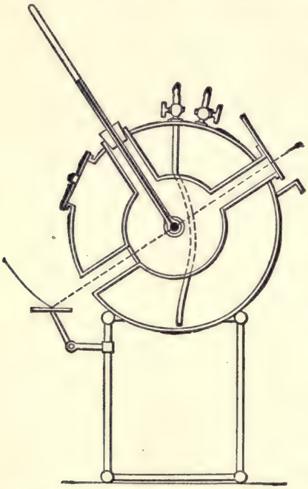

Fig. 92. Violle's Actinometer.

The establishment of the temperature equilibrium requires fifteen minutes, and the differences of temperature observed vary from 15° to 20°.

Violle found in this way, for the temperature of the sun, figures varying from 1500° to 2500°.

Pouillet and Violle made use of Dulong and Petit's law of radiation,

$$q = a^t,$$

that the discoverers had established by observations reaching only to 300°.

The constant a may be determined for each apparatus by a single experiment made at a known temperature. This law, as we shall show farther on, is not exact, so that, according to the temperature used to determine the constant, a different value of the latter is found, and consequently also different values at temperatures calculated, assuming this law to hold. This is the reason for the differences between the three figures, 1300, 1500, and 2500, of Pouillet and Violle. They correspond to determinations of the constant obtained by means of preliminary experiments made at the temperatures of 100°, 300°, and 1500°.

The elder Secchi, making use of Newton's formula,

$$q = a(t_1 - t_0),$$

still more inexact, found for the sun's temperature several millions of degrees.

Work of Rosetti. — The Italian scientist, Rosetti, was the first to grasp the fundamental importance of the choice of the law assumed for radiating power; he showed that a graduation made by an experiment at 300° gave for the temperature of a body heated in the oxyhydrogen flame:

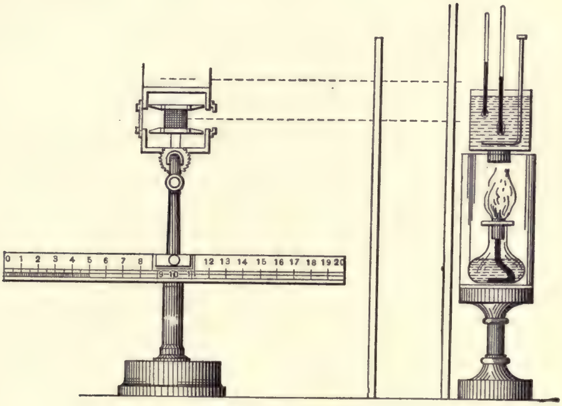

Fig. 93. Rosetti's Apparatus.

46,000 if one uses the law of Newton;
1,100 if one uses the law of Dulong and Petit.

Now the temperature of the oxyhydrogen flame is about 2000°.

This physicist used a thermoelectric pile whose sensibility could be changed without touching the element; in the apparatus of Violle it is necessary, on the contrary, to change the thermometer, a proceeding which renders the observations comparable with difficulty.

The pile (Fig. 93) consists of twenty-five sheets of bismuth and antimony; these sheets are very thin, for the whole of the apparatus is but 5 mm. on a side. The whole is inclosed in a small metallic tube.

To make an experiment, there is placed before the pile a screen filled with water, which is removed at the instant of taking an observation.

A preliminary calibration made with a Leslie's cube of iron filled with mercury that is heated from 0° to 300° gave the following results:

Excess of the temperature of the cube over the surrounding temperature.	Reading of galvanometer.
32.8°	10.0°
112.8	55.0
192.8	141.9
272.8	283.5

Newton's law and that of Dulong and Petit giving no concordance between the numbers observed and those computed, Rosetti proposed the formula

$$Q = aT^2 (T - \theta) - b (T - \theta),$$

where T = absolute temperature of the radiating body, θ = the absolute temperature of the surroundings. This formula with two parameters permits necessarily a closer following of the phenomenon than a formula with but a single parameter.

$T-\theta$.	Deflections observed.	Deflections computed. Dulong's law.	Rosetti's law.
50	$A =$ 17.2	$A+2.12$	$A-0.23$
100	46.4	+0.95	....
150	90.1	−2.12	+0.70
200	151.7	+4.82	+0.99
250	234.7	+2.83	−0.12

Rosetti showed later that the formula he proposed did not lead to absurd results for higher temperatures. A mass of copper was heated to redness in a flame, and the temperature was estimated by the calorimetric method (a quite uncertain method, as the variation of the specific heat of copper was not known). The two methods gave respectively 735° and 760°. This difference of 25° is less than the experimental uncertainties.

Disks of blackened metal placed in the upper part of a Bunsen flame gave, according to the formula, temperatures of the order of 1000°; oxychloride of magnesium in the oxyhydrogen blast lamp gave 2300°. All these numbers are possible.

Rosetti, using this formula, found 10,000° for the temperature of the sun, this figure resulting from an extrapolation above 300°.

Modern Radiometric Apparatus. — The principles most often made use of in modern receiving apparatus for thermal radiation are:

1. The generation of an electric current in a circuit composed of two dissimilar metals by the radiation which falls on one or more junctions, or the *thermopile* of Nobili, often called the Melloni thermopile, which we have just seen was used by Rosetti, and which has been in use for nearly a century, and in recent years rendered very sensitive.

2. The increase in resistance of a metallic strip, forming one or more branches of a Wheatstone bridge, due to the rise in temperature caused by the incident radiation, or the *bolometer* of Langley.

3. The deflection, by radiation, of vanes delicately mounted in vacuo, — the *radiometer* of Crookes.

There have been modifications and improvements in all of these types of apparatus, some of which we shall mention briefly, such as the combination of the thermopile and moving-coil galvanometer known as the *radiomicrometer*, due to d'Arsonval and Boys independently. They can all be used to measure temperatures when once calibrated in terms of black-body radiation, with the limitations already described in the preceding chapter or applications of the radiation laws.

It should perhaps also be emphasized at this point that for a strict application of the laws of radiation of the black body to such apparatus, not only the radiation source but also the receiver should be black. Plane surfaces covered with lamp- or platinum-black are an approximation to this condition, which may be still more closely realized, when possible instrumentally, by making the receiver conical, as done by Féry; or better, a hollow sphere with small opening, as attempted by Mendenhall; or by inclosing the sensitive portion of the receiving apparatus within a sphere brightened on the inside, as was done by Paschen; or finally, within a diaphragmed cylinder, such as used by Langley and Abbot. All of these forms of apparatus are rendered more sensitive by mounting in vacuo, and the radiometer can hardly be used otherwise; but there ensues the complication of the selective absorption of the window, which may become serious when extrapolating for high temperatures, especially if total radiation is used. The radiation of a narrow spectral band may also be used with all such apparatus, but this cuts down the sensibility enormously, and this method is hardly practicable for temperature measurements, except perhaps in very special cases in the laboratory.

Very little work has been done until recently with radiometric apparatus on the estimation of terrestrial temperatures, due perhaps to the existence of other methods of sufficient accuracy and sensibility; the radiometric methods being in practice largely reserved for investigation of the radiation characteristic of various substances at high temperatures and for the estimation of the temperature and spectral radiation of the sun, especially in the infra-red. The possibility of rendering the radiometric methods recording and the recent development of simple types of apparatus have given an impetus to their use in temperature measurements. As to the ultimate sensibility attainable with the various types of apparatus mentioned above, comparative examination by Coblentz has shown that there is very little choice in the matter, although each apparatus has its characteristics which render it more fit in certain classes of problems than the others.

The Thermopile. — This instrument was the earliest to be used in radiometric work, and its principle is, as we shall see, the only one, of those above mentioned, actually used in the construction of an instrument primarily designed for high-temperature measurements radiometrically. Types of multiple thermopiles are illustrated in Fig. 94. In *a* is shown the linear thermopile of Rubens of 20 junctions of 1 mm. constantan of wire about 0.1 mm. diameter with an exposed area of about 0.8 by 20 mm. The resistance can be cut down by shortening the connecting wires and the heat capacity and conduction lowered by using thinner wires of say 0.06 mm., and by making the unexposed junctions smaller than the others. These modifications, shown in *b*, are due to Coblentz. For sources of small area the form *c* may be used. A sensitive galvanometer is required whose best resistance for highest sensibility is that of the thermopile.

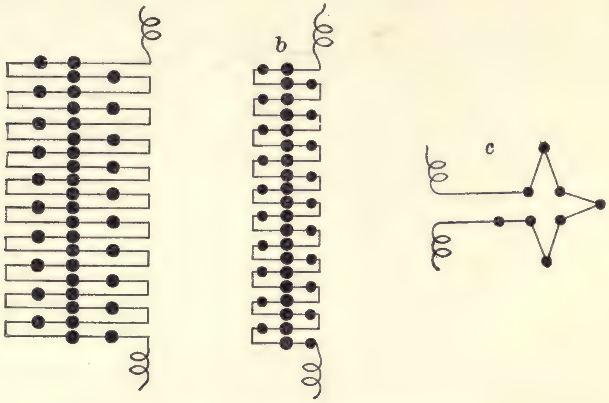

Fig. 94. Multiple Thermopiles.

Callendar has recently suggested several radio-balances for measuring radiation in absolute measure, which are suitable in certain forms for high-temperature measurement. Among these is his disk radio-balance (Fig. 95), in which heat supplied by radiations is directly compensated by the Peltier absorption of heat in a thermojunction, 1, through which a measured electric current is passed. In the simplest form of the instrument, radiation admitted through a measured aperture 2 mm. in diameter falls on a small copper disk 3 mm. in diameter by 0.5 mm. thick, to which two thermojunctions are attached, forming a Peltier cross. One couple is attached to a sensitive galvanometer *G* for indicating changes of temperature. The other is connected to a battery B and rheostat R in series with a milliammeter or potentiometer for measuring the current required to reduce the deflection of the galvanometer to zero. If A is the area of the aperture in $\overline{\text{cm.}}^2$, H the intensity of radiation received in watts per $\overline{\text{cm.}}^2$, a the absorption coefficient of the surface of the disk, P the Peltier effect in volts ($P = T\frac{dE}{dT}$ when T = absolute temperature and $\frac{dE}{dT}$ the thermoelectric power), C the balancing current in amperes, and R the effective resistance of the couple, the equation giving the value of the radiation in absolute measure is

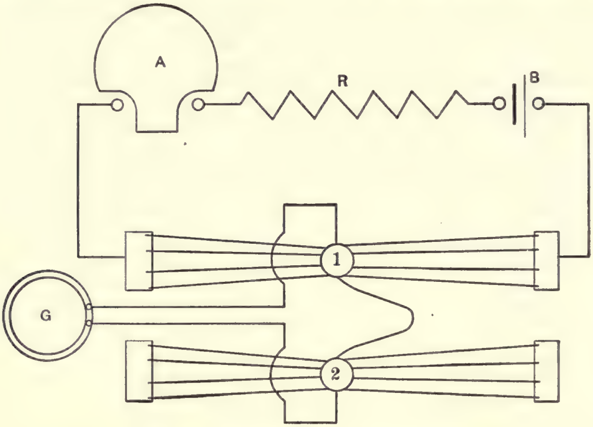

Fig. 95. Callendar's Radio-balance.

$$aAH = PC - C^2R.$$

The value of R in the small correction term for the joule effect is readily determined by observing the neutral current $C_0 = \frac{P}{R}$, for which the joule effect balances the Peltier effect. In practice, two similar disks with similar connections are mounted side by side in a thick copper box, and are balanced against each other in order to avoid changes of zero due to exposure to stray radiation, sunshine, or to rapid variations of temperature. For the measurement of temperature with such an instrument, H may be expressed in terms of the emissivity, distance, and temperature of the source, or the instrument may be calibrated empirically by means of a black body.

The Radiomicrometer. — We may illustrate the use of this instrument for temperature measurements by describing the experiments of Wilson and Gray. These physicists measured the intensity of radiation by means of a thermoelectric couple, a method first conceived by Deprez and d'Arsonval. A movable coil made of two different metals (silver and palladium) is suspended by a silk cocoon fiber between the poles of a magnet. The solar radiation is allowed to fall upon one of the junctions, while upon the other junction is directed a source of heat which exactly balances the first. As the temperature of this auxiliary source is necessarily the lesser, it is necessary that the apparent angle which it subtends at the galvanometer be the greater.

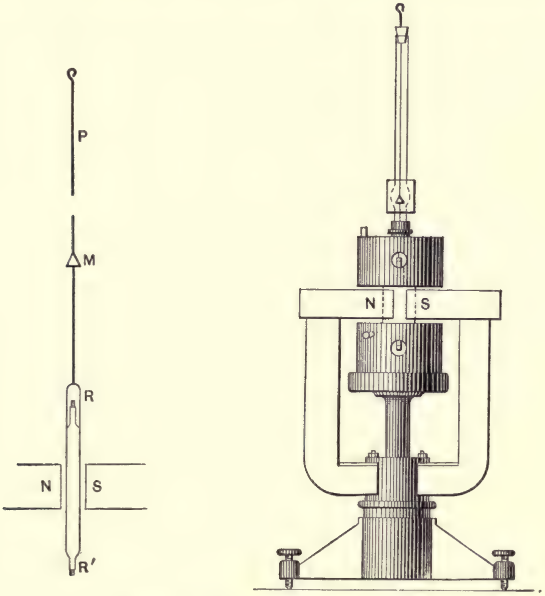

Fig. 96. The Radiomicrometer.

Wilson and Gray used an apparatus similar to the radiomicrometer of Boys. The suspending fiber is of quartz; the metals employed are bismuth and antimony. The electromotive force so produced is twenty times greater than that obtained with the palladium-silver couple. The metallic strips R and R' (Fig. 96) are very thin (0.1 mm.), which renders the construction of the apparatus quite delicate. In order to protect the movable coil against air currents, it is inclosed in a metallic case; an open tube lets pass in the radiation; diaphragms set inside this tube prevent air disturbances.

Instead of measuring, as may be done, the deflection of the mobile parts, these observers preferred to employ a null method making use of another radiation, that from a modification of the *meldometer* of Joly, an apparatus used also for the calibration of the radiomicrometer. The meldometer (Fig. 128) consists of a strip of platinum heated by an electric current; the dimensions are as follows: 102 mm. in length, 12 mm. in breadth, and 0.01 mm. thick. This strip they placed in the midst of an inclosure surrounded by water. Fastened at one end, it is held in place at the other end by a spring and carries on this end a lever to which is fixed a mirror arrangement serving to optically amplify the variations in the length of the strip resulting from its heating by the passage of the more or less intense current.

The relation between the change of length and the temperature is determined by means of the fusion of very small fragments ($\frac{1}{10}$ milligram) of bodies whose fusing points are known. Wilson and Gray used the following, which for the gold and palladium are certainly too low:

Silver chloride	452°
Gold	1045
Palladium	1500

With this apparatus they apparently verified, up to the fusion of platinum, the law of radiation given by Stefan:

$$E = \sigma (T^4 - T_0^4).$$

For the purpose of graduation, the meldometer was removed to a distance, so that its action on the radiomicrometer was always the same, and it was assumed that the intensity varies as the inverse square of the distance. It is besides necessary to know the emissive power of platinum; Wilson and Gray took as starting points the results given by previous experiments:

$t°$	Emissive power.
300°	$\frac{1}{5.4}$
600	$\frac{1}{4.2}$
800	$\frac{1}{3.9}$

And by extrapolation they found $\frac{1}{2.9}$ at the temperature of 1250°, the temperature which balanced the solar radiation with the somewhat large apparent angle subtended by the meldometer. In admitting, then, with Rosetti and Young, a zenith absorption of 30 per cent, the temperature of the sun, supposed to be a black body, was found equal to about 5900° C.

This figure, although reasonable numerically in the light of later work, must be considerably uncertain, on account of the errors involved in the fusing points employed for graduation, and because of the fact that the radiation from platinum does not obey Stefan's law. Furthermore, the constants for platinum were found in terms of those of copper oxide, a substance they found, incorrectly, to depart more from a black body than polished platinum.

Wilson has also given 5500° C. as the best result from his own experiments, using a black body as comparison source. Wilson and Gray also found the temperature of the carbon arc to be 3330° C., a result now known to be considerably low (see Chap. XI).

The Bolometer. — Although the principle of measuring the intensity of radiation by the change in resistance of a metallic strip had been used by several observers before Langley, he nevertheless deserves the credit for first constructing a practical instrument and developing it to a very high state of sensibility. There have been several types of bolometer used, although in all of them the Wheatstone bridge method of measuring resistance is employed. For spectrophotometric work, usually two narrow strips of extremely thin platinum serve as adjacent arms of the bridge; in the Smithsonian instrument used by Langley and Abbot, the strips are 12 mm. long, 0.06 mm. wide, and so thin that the resistance is about 4 ohms; the measuring current is 0.03 milliamperes. The measurements are the same as those with the resistance thermometer used with a bridge, and, in special work, an extremely sensitive galvanometer, usually a Kelvin multiple-coil instrument of low resistance, short period, and the highest possible current sensibility, 10^{-10} to 5.10^{-11} amperes per mm. at 1 m. A spectrometer of proper design is of course also essential in spectral radiation work.

For measurement of the total energy, the grid form, or surface bolometer, such as used by Lummer and Kurlbaum in their verification of the radiation laws, is preferable. In their instrument, they had four similar bridge arms of platinum foil composed of 12 connected strips 32 by 1 mm. and 0.001 mm. thick; two diagonal arms being placed one behind the other and exposed to the radiation. The highest temperature sensitiveness attained with the bolometer is 10^{-7} deg. C. per 1 mm. deflection. The portion of the instrument receiving radiation is inclosed within a well-screened and jacketed case, which may be evacuated if desired, and a lens or mirror used for concentrating the radiation.

In Callendar's form of absolute bolometer, which is of the grid or surface type, the intensity of radiation in absolute measure is determined by observing the value of the electric current required to produce the same rise of temperature in the grid as the radiation to be measured. Callendar has also introduced several instrumental improvements, such as automatic experimental compensation of that part of the grid not receiving radiation directly thus eliminating the creep in attaining a maximum. This instrument is also made self-recording. Callendar has also developed several modifications in bolometer design that may prove serviceable in temperature measurements, particularly when a relatively large area is available.

Although the bolometer does not appear to have been used as a pyrometer, it can readily be adapted for that purpose; and instruments of sufficient sensitiveness and robustness could readily be devised. They can of course be made self-registering.

The Radiometer. — This appears to be the least adapted for temperature measurements of the radiometric instruments we have mentioned. The apparatus consists of two blackened vanes

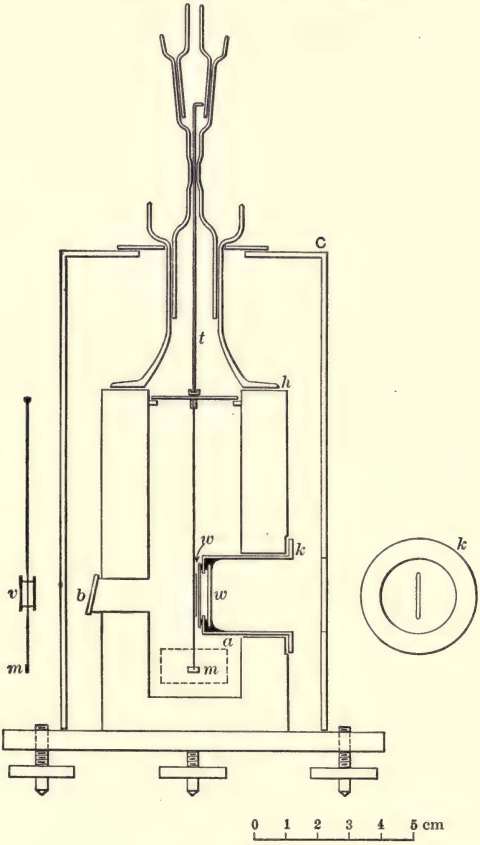

Fig. 97. Radiometer.

hung in vacuo on a fine quartz fiber (Fig. 97). Radiation falling on a vane deflects the suspended system, whose angle is read, as in the case of a galvanometer, with mirror, scale, and telescope. The readings are influenced by many factors, notably by the residual gas pressure, the location of the vanes, and the nature of the window. The instrument is not transportable and cannot be calibrated in absolute measure. Its sensitiveness is, however, very great.

Standard Pyrheliometers. — The International Union for Coöperation in Solar Research in 1905 adopted temporarily Ångström's compensation pyrheliometer as standard. In this instrument, radiation is received on a metallic strip, beside which, but shielded from the radiation, is a similar strip through which is sent a measured electric current of such strength that the temperatures of the two strips are the same, as measured by attached thermocouples. The assumption is then made that the strip carrying the current may be substituted for that receiving the radiation.

Calling Q the heat produced in gram calories per minute by the current, proportional therefore to the radiation intensity, r the resistance of the strip, and i the current, we have, following Ångström:

$$Q = \frac{60}{4.19} \cdot \frac{ri}{ba} = \text{const.} \cdot i^2,$$

where $a =$ absorbing power of blackened strip surfaces and $b =$ width of strips. The early instruments were made with platinum strips, but Callendar having shown that the temperature coefficient of this metal is a serious source of error, strips of manganin are now used. Ångström has used his pyrheliometer in a considerable number of laboratory investigations, including a study of the radiation from incandescent lamps and from the Hefner standard. The latter he determined to radiate $\frac{0.0147 \text{ gr. cal.}}{\text{mm. } \overline{\text{cm.}}^2}$.

As used by Callendar, Abbot, and others, the Ångström instrument, compared with absolute radiometric apparatus, gives slightly too small values of radiation intensity.

At the Astrophysical Laboratory of the Smithsonian Institution, Abbot and Fowle have recently devised an absolute radiometric instrument composed of a black-body receiver combined with a flow calorimeter. V. A. Michelson in 1894 had also used a black-body receiver combined with a Bunsen calorimeter. A form of the Smithsonian standard pyrheliometer is illustrated in part in Fig. 98, in which *a* is the diaphragmed chamber with conical base for receiving the radiation which first passes through the blackened tube *b*, also supplied with diaphragms *c*, *c*, and an electromagnetically operated shutter *gh*. The water enters at e_1 and, after circulating over the walls *d* and *l* of the double water jacket, passes out at e_2 into an automatic weighing apparatus. At f_1, f_2, f_3, f_4 are the coils of platinum-resistance thermometers giving the temperature of the water before and after absorbing the radiation. The constants of the instrument are determined by placing a heating coil at *m* and measuring the input of energy electrically. It was found that the calorimeter recorded practically 100 per cent of the energy supplied by the heating coil.

Either of these pyrheliometers could be used to measure temperatures, and it is not impossible that an instrument of the latter type, or of Michelson's, may be of use in absolute pyrometric apparatus in those researches where it is essential that the receiver be a black body and where it may be desired to measure the radiation in absolute units. Secondary pyrheliometers have also been designed recently by Abbot, Marvin, and others.

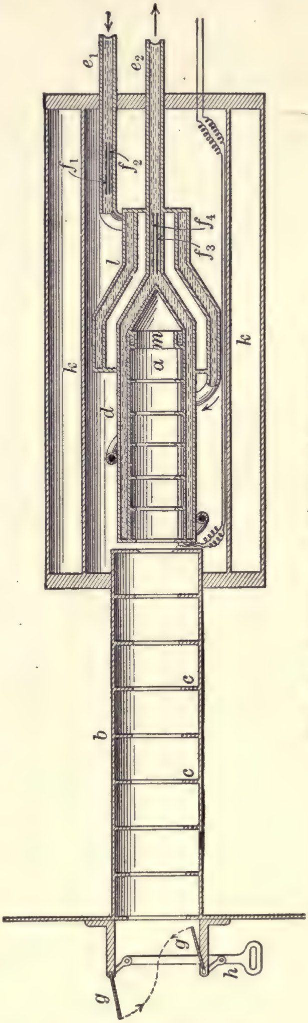

Fig. 98. Smithsonian Standard Pyrheliometer.

Thermoelectric Telescopes. — *The Féry pyrometer* was the first convenient form of instrument making use of total radiation and based on Stefan's law (page 245) to come into practical use for temperature measurements. As in the case of the photometric pyrometers, the limitations as to the realization of a black body apply here also with even greater emphasis, as an instrument using the whole spectrum, visible and invisible, is most sensitive to selective radiation effects.

Use is made of the Stefan-Boltzmann law,

$$E = \sigma (T^4 - T_0^4),$$

in the following way: Radiation from an incandescent body is focused upon a very sensitive thermocouple and raises its temperature. The electromotive force thus generated at the junction actuates a sensitive potential galvanometer in series with the couple in exactly the same way as in the Le Chatelier thermoelectric pyrometer; so that we have here a radiation pyrometer which is direct-reading by means of a pointer on a scale, and may therefore readily be made a recording instrument.

The difficulty in construction of such an instrument is realizing a material for lens which is transparent for all radiations visible and invisible, so that the pyrometer may be calibrated directly in terms of Stefan's law, and so that its indications will be reliable at temperatures however high. This is effected in the laboratory type of instrument by use of a fluorite lens which for temperatures above 900° C. satisfies the conditions of not altering appreciably the radiations transmitted through it; that is to say, the ratio of the radiations absorbed to the radiation transmitted is constant.

At low temperatures a large proportion of the energy exists in the form of long wave lengths, and as fluorite has an absorption band in the infra-red (near $6\,\mu$), it will absorb a considerable proportion of the radiation, and therefore Stefan's law can no longer be assumed.

Fig. 99 illustrates the construction of the original laboratory form of the instrument, where F is the fluorite lens, P a rack and pinion for focusing the radiations upon the thermojunction of iron-constantan, and protected from extraneous rays by the screens *C*, *D*, shown also in section at *AB*. The thermojunction is of exceedingly small dimensions, only a few thousandths of a millimeter wide, and is soldered to a silver disk. The leads are brought out to the insulated binding posts *b*, *b′*, so placed as to reduce the chances of extraneous thermal currents to a minimum. The circuit is completed through a sensitive galvanometer provided with a scale. A diaphragm fixed in size and position, *EE*, gives an opening of constant angle independent of the focusing, whereby the cone of rays striking the junction is not changed in size by focusing.

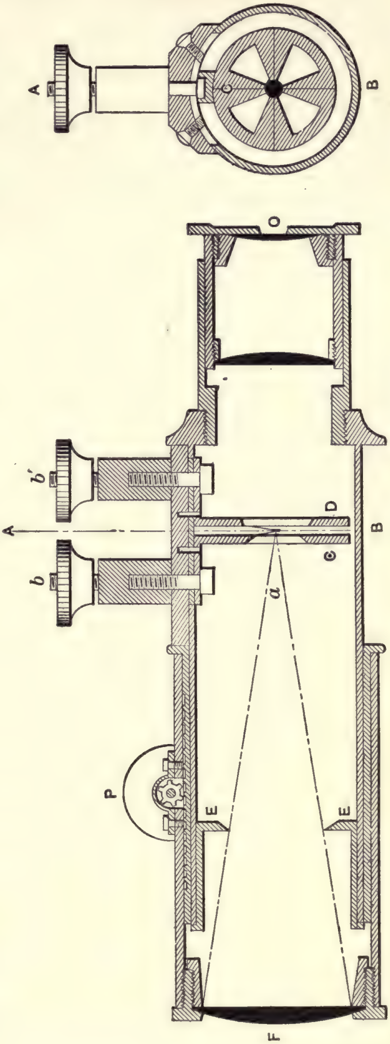

Fig. 99. Féry Telescope Pyrometer.

In making a temperature measurement, it is necessary to sharply focus the image of the incandescent object upon the thermojunction by means of the eyepiece *O*, and care must be taken that this image is of greater size than the junction. This adjustment once made, the pyrometer operates indefinitely while sighted upon the same object, and readings of the galvanometer scale give temperatures directly from the calibration.

The precision attainable with this form of instrument, over the range it may be controlled with the thermoelectric pyrometer, is shown from data obtained by Féry, assuming Stefan's law to hold in the form,

$$CE = d = 7.66\,T^4 \times 10^{-12},$$

where E is the total energy of radiation and d the galvanometer deflection and T the absolute temperature.

d.	Temperature from thermocouple.	Temperature from Stefan's law.	Δ in degrees.	Error in %.
11.0	844°	860°	+16°	1.85
14.0	914	925	+11	.84
17.7	990	990	0	.0
21.5	1054	1060	+ 6	.60
26.0	1120	1120	0	.0
32.2	1192	1190	− 2	.17
38.7	1260	1250	−10	.80
45.7	1328	1320	− 8	.60
52.5	1385	1380	− 5	.36
62.2	1458	1450	− 8	.50

It is evident, furthermore, that if the galvanometer has a uniformly graduated scale and the temperature T_1 corresponding to any one scale reading R_1 is known, that for any other reading R_2 may be found from the relation

$$T_2 = T_1 \sqrt[4]{\frac{R_2}{R_1}},$$

which also shows that errors in the galvanometer readings are divided by four when reduced to temperatures. For very high temperatures, deflections off the scale of the galvanometer will be obtained and the instrument will be excessively heated. Féry overcomes these difficulties by substituting a smaller diaphragm before the objective when the radiation is reduced in the ratio of the areas of the apertures.

The highest temperatures which may be estimated by this pyrometer are limited only by the applications of Stefan's law to this extreme region, and whether Stefan's law applies or not, consistent results, nevertheless, will be obtained.

Instead of the deflection galvanometer, it is better in work of precision to substitute a low-range potentiometer with sensitive galvanometer (see page 139).

The laboratory form of apparatus described above is not suitable for use in technical practice, and fluorite is difficult to get of sufficient size. An industrial pyrometer is readily made by substituting for the fluorite lens one of glass of wide aperture, and for the delicate galvanometer one of the same type and sensibility as used in thermoelectric work; the resulting instrument is robust and sufficiently sensitive for all practical uses, and as made has a range of from 800° to 1600° C., although the upper limit could readily be extended by having two scales on the instrument, provided with a diaphragm.

The indications of the industrial form of this pyrometer will not obey Stefan's law exactly, but the instrument may readily be calibrated by direct comparison either with a thermocouple or with a laboratory form of Féry instrument, and the scale of temperatures engraved on the instrument. Both types of instrument can be used to reach lower temperatures (650°) by means of more sensitive galvanometers.

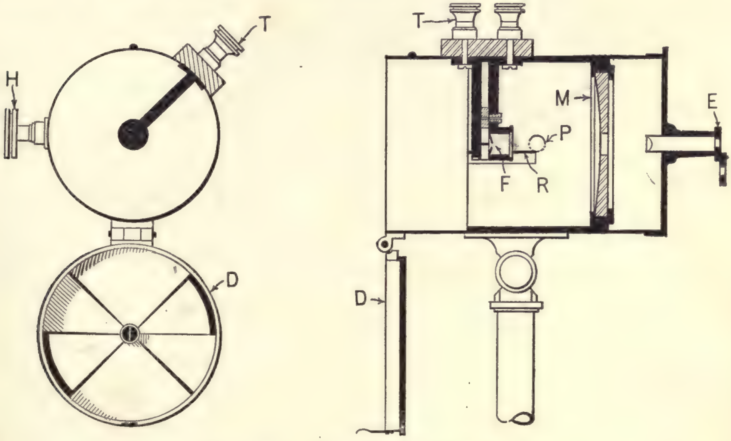

Fig. 100. Féry Mirror Telescope.

Féry Mirror Telescope. — This instrument (Fig. 100) was designed by Féry to replace both the laboratory and technical forms of lens telescope, and has been used very considerably in scientific and industrial work. As usually constructed the mirror is of gold on glass, and there is further provided an ingenious optical focusing device by means of which straight lines appear broken (Fig. 101), unless the instrument is in focus. The range of the instrument is increased by means of a sectored diaphragm, so that temperatures from the lowest to the highest may be read, although for reading the lowest temperatures with any considerable precision a quite sensitive galvanometer is needed, or a more sensitive thermocouple may be used to produce the same effect.

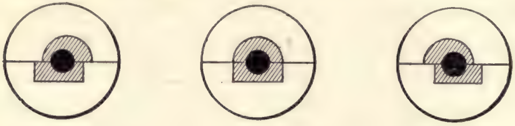

Fig. 101. Focusing Device.

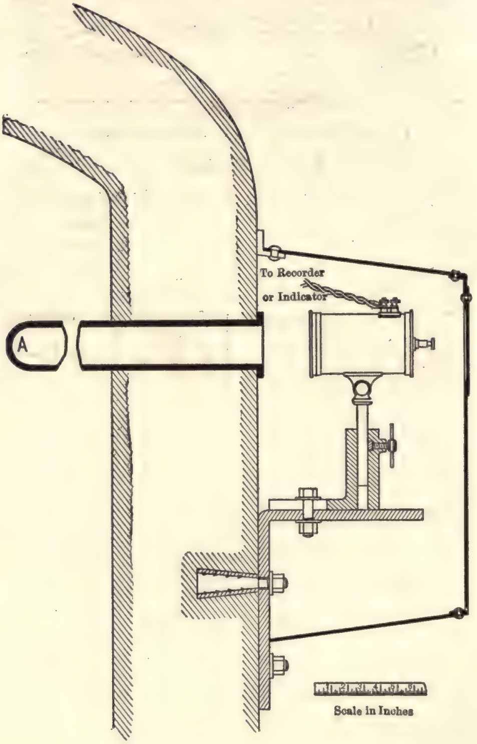

Fig. 102. Mounting on Kiln.

The potentiometer method of reading for very accurate work may of course be substituted, as with the other forms of telescope. The robustness of the instrument has recently been increased for industrial work by substituting pivot galvanometers for the delicate suspended-coil instruments hitherto used. The gold mirror may be considerably tarnished without seriously influencing the readings; and if the aperture of the furnace sighted upon is of sufficient size and the telescope in focus, the temperature readings are practically independent of the distance. The instrument takes its final reading very promptly with only slight creep. The readings of the instrument appear to be influenced somewhat by the area sighted upon and by the temperature of the region immediately outside the central cone of rays, or in other words, by stray radiation. For example, a Féry pyrometer, sighted into and clear through a resistance-tube furnace of 75 mm. aperture open its whole length with no diaphragm, will register several hundred degrees if the walls of the furnace are at 1100° C. An aperture of about 1-inch-wide opening per 1 yard of distance (2.5 cm. per 1 m.) is required for the usual industrial instruments. A suitable mounting for determining

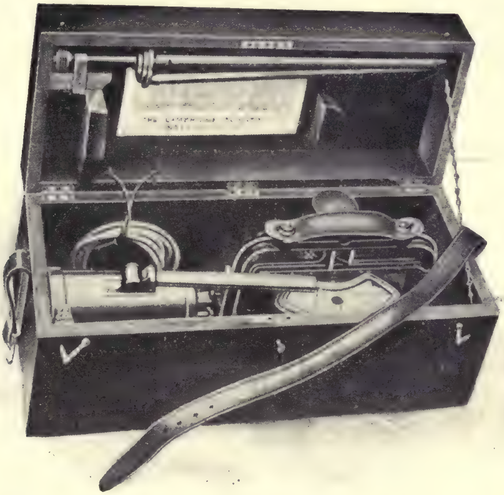

Fig. 103. Telescope and Galvanometer in Case.

the temperatures of a kiln is shown in Fig. 102. A Féry pyrometer packed in its case with portable galvanometer mounted in gimbals is shown in Fig. 103.

Féry's Spiral Pyrometer. — Another method of registering the radiation focused by the telescope mirror has been devised by Féry, Fig. 104. The thermocouple and galvanometer are replaced by a bimetallic spring *S* placed at the mirror focus, carrying an aluminium pointer *P* which turns over a dial *D* graduated in degrees of temperature in response to the differential expansion of the spring when radiation is concentrated upon it. This instrument, therefore, has no accessories, and, in spite of a zero creep and set difficult to eliminate in the spring, this form of instrument may serve satisfactorily for many industrial uses where a moderate precision is desired.

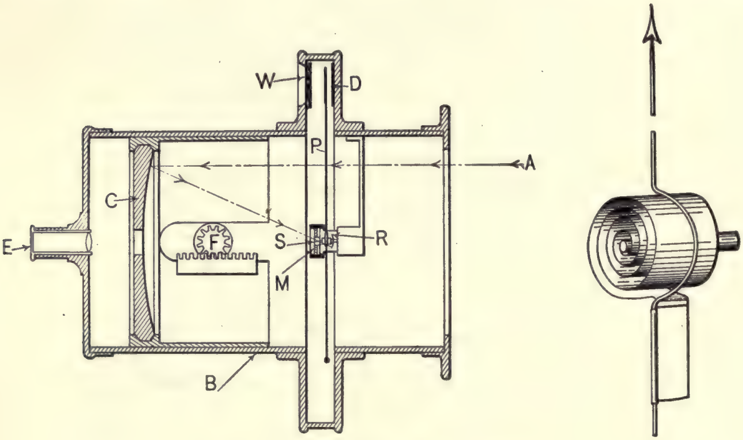

Fig. 104. Féry Spiral Pyrometer.

Other Radiation Pyrometers (Thwing, Foster, Brown). — In Thwing's apparatus the reflecting mirror is replaced by a bright cone which by multiple reflection concentrates the radiation at its apex on one or more thermocouples in series with a portable galvanometer. This apparatus requires no focusing, but has to be sighted along the outside of the tube or adjusted in the direction until the reading of the galvanometer is a maximum when the area sighted on is not large. Different sized apertures may be used at the open end to give different temperature ranges. Foster has also transformed the Féry telescope into a "fixed-focus pyrometer" (Fig. 105), by putting the thermocouple *D* and the aperture *EF* at the *conjugate foci* of the gold mirror *C*. A considerable area is required to sight upon. This instrument has to be pointed also by trial. In a similar instrument recently issued by the Brown Pyrometer Company, the sighting of the instrument is facilitated by the use of a finder such as used with photographic cameras.

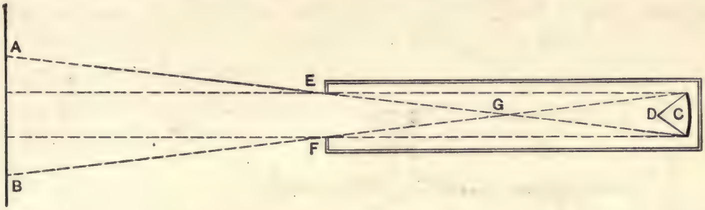

Fig. 105. Fixed-focus Pyrometer.

The Féry pyrometer of constant-focus type has been coupled directly to a long closed-end tube by Whipple, thus rendering the instrument's readings independent of the nature of the furnace or material of which the temperature is sought, since the closed end tube is plunged directly into the hot region or melted metal to a sufficient depth, and the pyrometer proper is always focused on the bottom of this tube and indicates its temperature.

Mr. Whipple has used this instrument successfully for taking molten steel and brass temperatures in the crucible at temperatures for the former as high as 1550° C. The material of the extension tube will depend on the medium into which it is thrust.

All of the total-radiation pyrometers can be made self-registering by simply substituting for the indicating galvanometer a suitable recording instrument. The Féry mirror telescope is commonly used with the Cambridge thread recorder (Fig. 152).

Some Experimental Results. — To call attention to the scope of application of the radiation pyrometer, we may note some of the investigations carried out with one or another of its forms.

We have already cited the early attempt at an estimation of the sun's temperature by this method, and we shall return to this matter in the chapter on standardization, as well as to measurements on the temperature of the carbon arc with the Féry pyrometer.

Using his pyrometer, Thwing has measured the total emissivity (page 258, equation Ba) of streams of molten iron and copper. For cast iron in the liquid stream at 1300° to 1400° C., the intensity of radiation was found to be 0.29 that of the solid metal at the same temperature, and for mild steel at 1600° to 1650° C., the value was 0.28. These values appeared to hold to 1800° C. For copper Thwing finds the emissivity 0.14 that of a black body. Burgess, with a Féry mirror pyrometer, finds for copper $E_x = 0.15$, and for copper oxide $E_x = 0.60$, approximately. The observations of Burgess satisfy the following equations:

For liquid copper: $t = 3.55 F - 1018;$
For cuprous oxide: $t = 1.41 F - 169;$

when t is the true temperature centigrade, and F the reading of the Féry pyrometer calibrated in terms of the radiation from a black body. It will be seen that at 1083° C., the melting point of copper, the Féry instrument reads some 490° low when sighted on a clear surface of pure copper. A Féry pyrometer sighted on copper oxide at 700° C. will read higher than when sighted on an oxide-free surface of liquid copper at 1100° C. A similar interpretation of Thwing's results on iron shows that at 1520° C., for example, the melting point of pure iron, a radiation pyrometer sighted on the clear metal would read about 370° low, assuming $E_x = 0.29$ for pure iron. These illustrations are sufficient to show that, with a total-radiation pyrometer, true temperatures are given only under carefully specified conditions.

Conditions of Use. — It will be noticed that among the types of apparatus described in this chapter, there has been but one, the thermopile, in its several forms of thermoelectric telescope, which has as yet been used as a pyrometer. We have seen, however, that several of the other types of radiometric apparatus may also readily be made to serve the purpose of temperature-measuring instruments, and that some of them may in certain cases offer theoretical and practical advantages over other forms of pyrometer.

In many industrial operations the temperatures are so high that no substance usable as an active part of a pyrometer, not even platinum, can resist for long their action or that of the chemical agents present. When it is desired, therefore, to have apparatus of continuous indications, or with which readings may be obtained without intervention of an observer, and at the same time unalterable by heat, it is necessary to resort to radiation pyrometers. That with them temperatures may be read off a robust form of portable millivoltmeter, and that such instruments are readily made self-registering, are also matters of great practical convenience.

It should be emphasized, however, that in general such pyrometers sighted upon objects in the open air will read too low in temperature, due to the selective radiating properties of all materials, although radiation pyrometers may be calibrated to give true surface temperatures sighted upon any substance whose radiating properties (page 259) are known; and in any case a self-consistent but arbitrary scale is obtained so long as the surface sighted upon does not change its emissivity. Fortunately, in many industrial operations, these limitations are easily overcome as well as others. Flames and furnace gases, which also affect seriously the readings of such pyrometers, may be avoided, together with the selective radiation errors, by sighting on the bottom of a closed-end tube inserted into the furnace. For example, a tube of fire clay or magnesia, or other material which will stand the temperature and chemical actions present, passing through the lining of the furnace, and penetrating into the midst of the latter for a distance of 0.5 to 1.0 mm., closed at the inner end and open at the outer, would give a radiating surface at the temperature of the furnace (Fig. 102), and would approach very closely to the ideal black-body conditions under which the radiation instruments will read correctly whatever be the nature of the object sighted upon at the bottom of such a tube. The radiation laws in their simplest form apply quite exactly to such a radiating tube, so that if the pyrometer has been calibrated by sighting it upon a black body, the calibration will hold for sighting into this tube, or when sighting through a small aperture into any clear, closed space at constant temperature. The closed-end tube above mentioned may evidently be used in hardening baths and in many other kinds of industrial installations.

Care has to be taken, in setting up and using any radiation pyrometer, that one allows sufficient area to sight upon. This is illustrated in Figs. 105, 106, and 107. The opening of the furnace *F* must be large enough so that the cone between *M* and *D* is not cut into if the instrument *T* is focused on *D*. A smaller opening is allowable if *T* is focused on some such plane as *A* (Fig. 106), when the furnace is at a uniform temperature.

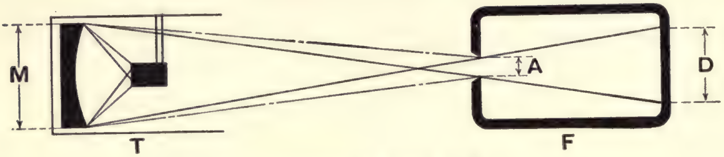

Fig. 106. Focusing on back of Furnace.

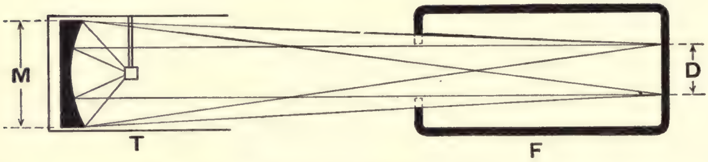

Fig. 107. Focusing on front of Furnace.

Calibration. — It is a difficult matter to calibrate satisfactorily a total-radiation pyrometer to very high temperatures, and this is particularly true of most of the industrial types. Thus relatively large apertures are usually required, which necessitates correspondingly large furnaces, over whose visible area a constant temperature is to be maintained, and measured by some auxiliary calibrated instrument such as a thermoelectric, optical, or standard radiation instrument. With a large enough diaphragm to sight upon at the center of a uniformly wound electric resistance furnace, unless great care is taken in the adjustments, there may exist, for example, differences of 30° to 50° C. between the two walls of a 2 mm. thick diaphragm as measured by thermocouples.

The total-radiation pyrometer is extremely sensitive, much more so than the optical instruments using a single color, to the lack of blackness, or to selective emission, in the source sighted upon; and this, combined with the large aperture requirement, complicates the problem. Furthermore, as the readings of these instruments are considerably influenced by the presence of flames, furnace gases, and dust, it is highly desirable to have a clear furnace to sight upon. While temperatures to 1400° or 1500° C. that are exactly measurable are obtainable in large electric resistance furnaces wound with platinum on porcelain, or in pots of metals with closed-end tubes inserted in the liquid or solid metal, no entirely satisfactory method of direct calibration free from the above sources of error to, say, 2000° or even 1700° C. appears to have been devised. Suitable iridium-tube furnaces lined with a glaze preventing evaporation of the iridium inwards could be constructed for use to 2000° C., but the cost of large enough furnaces of this type would be excessive and their life short. Carbon-tube furnaces lined with the available forms of magnesia or alumina are not satisfactory, due mainly to the porosity of the lining. This, perhaps, may be overcome by building such furnaces so as to prevent diffusion inwards by regulating the gas pressure from the center outwards. The presence of any kind of window before a total-radiation instrument, especially if it is to be used as a standard, is inadmissible, due to the unknown effect of the window absorption on the pyrometer readings. On the other hand, this type of pyrometer cannot be mounted in vacuo for calibration, as its readings would then differ from those obtained in air, due to different convection, radiation, and conduction conditions about the receiver.

From the fact that the usual forms of industrial instrument do not, in general, obey Stefan's law exactly, and often not even approximately, it is not with overconfidence that any considerable extrapolation of their temperature scales may be resorted to.

If a standard total-radiation instrument can once be calibrated satisfactorily in any laboratory, however, to very high temperatures, it will then be an easy matter to compare with it any other such pyrometers by sighting on any source of radiation whatever with the two instruments simultaneously.

It is perhaps proper to remark that these difficulties of realizing suitable calibration conditions impose equal uncertainties in the indications of such instruments as ordinarily used in practice.

The computation of a calibration is readily made by graphical methods. The equation $E = aT^n$, in which E is the E.M.F. generated for the absolute temperature T of a black body, and a and n are constants, represents well enough for most purposes the behavior of thermoelectric instruments of the Féry type. Plotting log E against log T gives us a straight line, so that only two points are absolutely necessary for calibration if the scale of E is correct and a strictly potential scale of E.M.F.'s. When a diaphragm is used for getting the higher temperatures, one observation combined with the two previous ones will suffice theoretically, as this second straight line should be parallel to the first. In practice this is very nearly but apparently not quite the case, due to extraneous heating and differences in behavior with the diaphragm in place and removed, so that there is some element of uncertainty in extrapolating by the above procedure.

Pyrometric telescopes may be most accurately calibrated by the potentiometric method (p. 135), when their readings are independent of the resistances of thermocouple circuit and galvanometer.

CHAPTER VIII.

OPTICAL PYROMETER.

Principle. — Instead of using the totality of the radiant energy, as in the methods described in the preceding chapter, use is made of the luminous radiations only. This utilization may be effected in many different ways, which give methods of unequal precision and varying in facility of manipulation.

Before beginning their study, it may be well to recall and illustrate certain properties of monochromatic radiation.

Properties of Monochromatic Radiation. — An incandescent body emits radiations of different wave lengths. For a given wave length and a given temperature, the intensity of this emitted radiation is not the same for different bodies: this is expressed by saying that they have for this radiation different *emissive powers*. Similarly, a body which receives radiations of a given wave length absorbs a part of them and sends back another part by diffusion or reflection; a certain quantity may also traverse the body. The *diffusing*, *reflecting*, or *transmitting* power at a given temperature, for a given wave length, varies from one body to another. The *emissive power and the diffusive power* (in the case of an opaque and nonreflecting body) *vary always inversely, resting complementary to each other*.

Substances of great emissive power, as lampblack, have a small diffusive power; substances of small emissive power, as polished silver and magnesia, have a very great diffusing or reflecting power.

If we take as the measure of the emissive power the ratio of the intensity of the radiation of the object considered to that of a black body (page 239) at the same temperature, and as measure of the diffusive power the ratio of the intensity of the radiation diffused to the incident radiation, the sum of these two quantities is equal to unity (see page 243).

The emissive power of a body varies from one radiation to another, and consequently also its diffusing and transmitting powers, since these two powers are complementary to each other. It follows that the relative proportions of the visible radiations received or given off by a body are not the same; so that different bodies, at the same temperature, appear to us to be differently colored.

At the same temperature, the color proper to a body, and its apparent color when it is lighted by white light, are complementary to each other. Yellow substances, as oxide of zinc heated, emit a greenish-blue light. At temperatures less than 2000° the red radiations predominate greatly and mask the inequalities of the radiations of other wave lengths. To render easily visible the colorations of radiating bodies, it is necessary to compare them with those of a black body under the same temperature conditions. A hole pierced in the body, or a crack across the surface, gives a very good term of comparison to judge of this coloration.

The intensity of the radiations emitted by a black body increases always with the temperature, and the more rapidly as we approach the blue region of the spectrum; but, on the other hand, the radiations from the red end are the first to commence to have an intensity appreciable to vision, so that the color of bodies heated to higher and higher temperatures starts with red, tending towards white, passing through orange and yellow. White is, in fact, the color proper to bodies extremely hot, as is the sun.

Bodies not black (the word " black " always being used in the sense of Chapter VI, page 239) have a law of increase different from that for black bodies, because the emissive power varies with the temperature. It increases unequally for the various radiations, so that the color of bodies, with respect to the color of a black body, changes with the temperature.

The following table gives for different colors the ratios of the values of emissive powers of some bodies to that of a black body as determined by Le Chatelier. The red radiation was observed through a glass containing copper, the green by aid of a chromium copper glass, the blue through an ammoniacal solution of cupric hydrate. The substance covered the junction of a thermoelectric couple, and was cut by grooves; and it was the brightness of the bottom of these grooves which was compared to that of the surface.

EMISSIVITIES (LE CHATELIER).

		Red.	Green.	Blue.
Magnesia	at 1300°	0.10	0.15	0.20
	1550	.30	.35	.40
Lime	1200	.05	.10	.10
	1700	.60	.40	.60
Oxide of chromium	1200	1.00	1.00	1.00
	1700	1.00	.40	.30
Oxide of thorium	1200	.50	.50	.70
	1760	.60	.50	.35
Oxide of cerium	1200	.80	1.00	1.00
	1700	.90	.90	.85
Auer mixture	1200	.25	.40	1.00
	1700	.50	.80	1.00

Values of the emissivities of metals and other substances are given in Table X of the Appendix.

Methods of Temperature Measurement. — The estimation of temperature, from measurements of luminous radiations, may, at least in theory, be made directly in three different ways, by utilizing:

The total intensity of the luminous radiation;
The intensity of a radiation of definite wave length;
The relative intensity of radiations of definite wave lengths.

In the chapter (VI) on the laws of radiation we have discussed the recent theoretical and experimental advances underlying these methods.

Measurement of Total Luminous Intensity. — The brightness of substances increases very rapidly with the temperature. One may with the unaided eye estimate comparatively this brightness, but this measurement is very uncertain, for lack of a constant standard of comparison. The sensitiveness of the eye varies, in fact, with the individual, with the light which the eye received immediately preceding, and with the attendant fatigue. Photometric processes, precise for comparison with a standard source, cannot be employed on account of the change of hue with the temperature.

The following method might be tried: Trace on a white surface, diffusive or translucent marks, of definite intensity and dimensions, and seek what fraction of the light must be employed to render the marks invisible. The indications will be still quite variable and will depend upon the degree of the eye's fatigue.

Nernst and others have made use of the empirical formula (A) of page 238,

$$\frac{I_1}{I_2} = \left(\frac{T_1}{T_2}\right)^x, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(A)}$$

connecting the total photometric brightness, expressed, for example, in Hefner candles, of a radiating body and its temperature. Rasch deduces theoretically the more general formula

$$I = I_1 \epsilon^{\alpha\left(1 - \frac{\theta}{T}\right)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(B)}$$

in which θ is the absolute temperature for which $I = I_1$. If I_1 is the brightness of the Hefner standard, we have per $\overline{\text{mm.}}^2$ of the luminous radiation from a black body, $\alpha = 12.94$ and $\theta = 2068$ abs. For small temperature differences (B) reduces to (A) if $xT = \text{const.}$ In view of the fact that several investigations involving considerable temperature differences have been based on the use of (A), it should be emphasized that (A) does not hold unless T_1 is very nearly equal to T_2.

Using (A) and taking the light from 1 $\overline{\text{mm.}}^2$ from a black body = 12.1 Hefners, when the two are of equal total photometric brightness, Nernst finds for the melting point of platinum 1782° and of iridium 2200° to 2240° C. Rasch, treating Nernst's data by (B) gets for iridium 2287° C. The same formulæ, it is interesting to note, apply also to monochromatic light, which amounts to saying that (A) and (B) used for total light give relations equivalent quantitatively, as shown by Rasch, to Wien's law for $\lambda = 0.542$, or approximately for the wave length of maximum sensibility of the eye, which is not a strictly constant quantity for different individuals nor for the same individual at different times. See page 255 and Fig. 88.

This method of using the total photometric brightness as a measure of temperature, therefore, lacks sensitiveness as well as definiteness, and is better replaced by methods based on the use of a single wave length.

Measurement of the Intensity of a Simple Radiation. — We may estimate the temperature of a body from the intensity of one of its radiations, provided that we know the emissive power of the body at that temperature and the law of variation of this radiation determined in terms of the gas thermometer.

The emissive power sometimes varies with the temperature, and generally is not known. It might seem that this would be enough to reject this method and similar methods by radiation. But this is not so, for the following reasons:

1. At temperatures higher than the fusing point of platinum there is no other pyrometric method at present applicable.

2. A great many substances have a considerable emissive power, nearly unity, and particularly some of industrial importance, as iron and coal.

3. The variation of radiation with temperature is sufficiently marked so that the errors committed in neglecting the emissive power are small. Thus at 1000° the red radiation emitted by carbon is quadrupled for an interval of 100°; it is doubled at 1500° for the same temperature interval.

Then, except for some bodies exceptionally white, the emissive powers at high temperatures are superior to 0.5. By taking them equal to 0.75, the greatest error that will be made for the ordinary temperatures comprised between 1000° and 1500° will be from 25° to 50°.

Furthermore, in cases where the emissive power is unknown, an optical pyrometer will still give a consistent temperature scale for a given body, i.e., in terms of black-body temperatures (page 242).

We shall now describe the ordinary types of optical pyrometer and their calibration and then indicate some applications.

Optical Pyrometer of Le Chatelier. — Ed. Becquerel had proposed in 1864 to refer the measurement of high temperatures to the measurement of the intensity of red radiations emitted by incandescent bodies; but this method had never been realized in a complete manner, and still less employed. Le Chatelier, taking up the question, devised an experimental arrangement suitable for such measurements, and he determined an empirical *law of radiation* of substances in terms of the temperature.

Photometer. — For these measurements a photometric apparatus is required which gives, not as do the ordinary photometers, a measurement of the total illumination produced by a source (illumination which varies with the dimensions of this source), but the intrinsic brightness of each unit of surface. Use may be made of a photometer based on a principle due to Cornu.

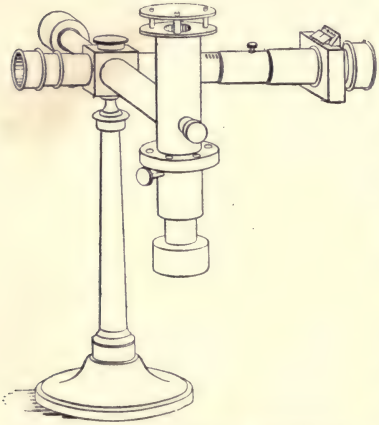

Fig. 108. Le Chatelier Pyrometer.

The apparatus (Figs. 108 and 109) consists essentially of a telescope which carries a small comparison lamp attached laterally. The image of the flame of this lamp is projected on a mirror M at 45° placed at the principal focus of the telescope. One adjusts for equality of intensity the images of the object that is viewed and of the comparison flame, these images being side by side.

The telescope comprises an objective in front of which is placed a cat's-eye diaphragm which admits of varying the effective aperture of this objective, and, beyond, a stand destined to carry tinted absorbing glasses.

At the focus of the objective is a mirror inclined at 45° which reflects the image of the lamp projected by an intermediary lens. An ocular, before which is placed in a set position a monochromatic glass, serves for observing the images of the flame and of the object.

To the lamp is fixed a rectangular diaphragm which stops the luminous rays not utilized and which carries a stand to receive tinted absorbing glasses.

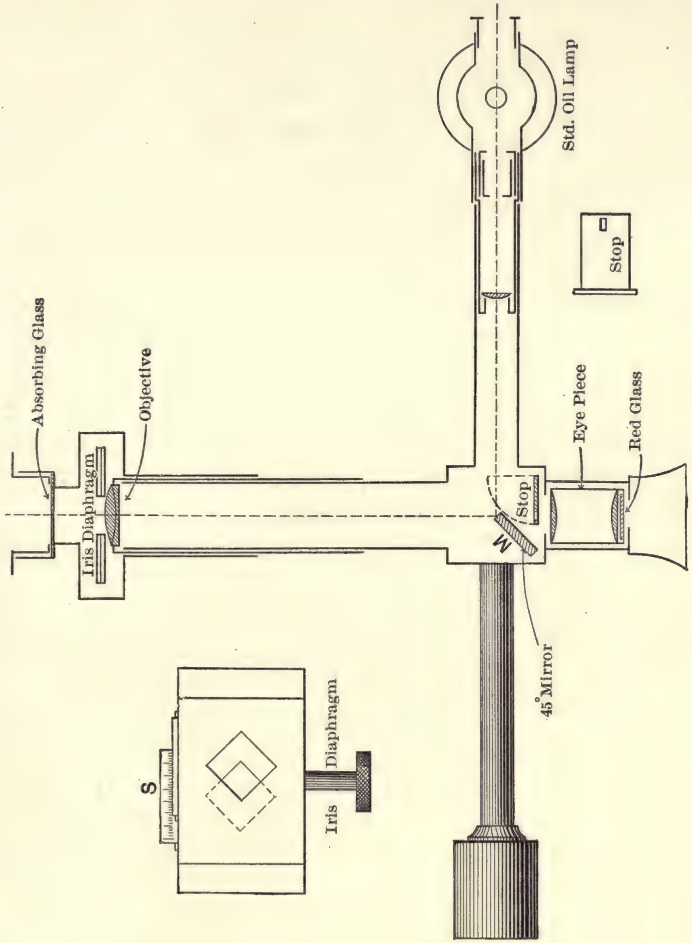

Fig. 109. Le Chatelier Pyrometer, Section.

The edge of the mirror at 45° is in the plane of the image of the source studied, so that the reflected image and the direct image are side by side, separated only by the edge of the mirror. This mirror, according to a method devised by Cornu, is made of a plate of black glass cut with a diamond, which gives a very sharp edge.

In order to vary the relative intensities of the images, one thus employs simultaneously tinted glasses placed before one or the other of the two objectives, and the cat's-eye mentioned. A screw allows of varying the aperture of this cat's-eye, and a suitable scale S indicates the dimensions of this opening.

It is very important that the tinted glasses have an absorbing power as uniform as possible and do not possess absorption bands. These conditions are fulfilled by certain smoked glasses of ancient make (CuO,Fe_2O_3,MnO_2); for the fabrication of these glasses use is now made of the oxides of nickel and cobalt, which give absorption bands.

To determine the absorbing power of these glasses, a measurement is made with and without them; the ratio of the squares of the aperture of the cat's-eye gives the absorbing power.

For monochromatic screens one may use:

1. Red copper glass, which lets pass $\lambda = 659$,* about. The use of red glass is preferable to the others, as it is more nearly monochromatic and because measurements at low temperatures may be made with it, the first radiations emitted being red.

2. Green glass ($\lambda = 546$, about). The observations are then easier than in the red for some eyes, but they can be commenced only at higher temperatures.

3. Ammoniacal solution of copper oxide ($\lambda = 460$, about). The use of this last screen, which is far from monochromatic, is without interest; the eye is only slightly sensitive to the blue radiations, and these last become somewhat intense only at high temperatures. Blue glass (Schott and Genossen, No. F 3875) is preferable.

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* Red glasses furnished by the maker Pellin, Paris, have an equivalent wave length of about $\lambda = 632$. Glasses which are more sharply monochromatic are furnished by Schott and Genossen of Jena, which firm also supplies very superior tinted absorption glasses; see page 335.

Adjustment of the Apparatus. — There are in the apparatus two parts which require very careful adjustment for best results, and these parts should consequently be so made as to admit of the necessary manipulation to obtain the desired effect.

1. The luminous beam coming from the lamp and which is reflected by the mirror, and that which comes directly from the object viewed, should penetrate into the eye in their totality. This condition is fulfilled if the images of the two objectives given by the ocular are superposed.

This is verified by examining with a lens these two images which are formed slightly behind the collar of the ocular. It is evidently necessary, in order to see them, to illumine the two objectives, one with the lamp, the other with any source of light. If the superposition does not exist, it is established by trial by turning the screws which hold the mirror. If it is not too severely jarred, the apparatus should remain indefinitely in adjustment.

2. In order that a steady light may be had, certain precautions in the adjustment of the comparison lamp are necessary. Le Chatelier recommends the employ of the same gasoline. The flame should have a constant height, equal, for example, to the window of the rectangular diaphragm placed before the flame. Its image should be cut exactly in two by the edge of the mirror, a result obtained by turning the lamp in its stand, which is eccentric (Fig. 110).

Finally, before taking an observation, it is necessary to wait some ten minutes for the lamp to come into heat equilibrium; then only does the flame possess a constant brightness.

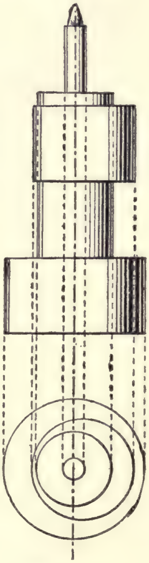

Fig. 110.
Mounting of Lamp.

Measurements. — In order to take an observation, a body selected as standard, as the flame of a stearine candle or the flame of a kerosene lamp, is examined; we observe:

1. n_0, the number of absorbing glasses;
2. d_0, the aperture of the cat's-eye;
3. f_0, the extension of the objective for focusing.

The same process is followed for the source to be studied, and the numbers n_1, d_1, f_1 are found.

k being the absorption coefficient of the tinted glasses, we have:

$$\frac{I}{1} = \left(\frac{1}{k}\right)^{(n_1 - n_0)} \cdot \left(\frac{d_0}{d_1}\right)^2 \cdot \left(\frac{f_1}{f_0}\right)^2.$$

For the glasses mentioned, the absorption coefficients are:

$k = \frac{1}{11}$, corresponding to $\lambda = 659$;
$k = \frac{1}{7}$, corresponding to $\lambda = 546$;
$k = \frac{1}{10}$, corresponding to $\lambda = 460$.

For very small objects which would have to be placed very near, a supplementary objective is put in front of the telescope; the object is placed in the principal focus of this new lens, the objective of the apparatus being focused for parallel rays. The absorptive power of this supplementary lens is reckoned as $\frac{1}{10}$.

Details of an Observation. — The first operation to make is the determination of the absorption coefficients of the absorbing glasses. For that, an object of suitable brightness is viewed once with the tinted glass before the cat's-eye and then without this glass. Let N be the aperture of the cat's-eye without tinted glass, and N' the aperture with such a glass. The coefficient k of absorption is

$$k = \left(\frac{N'}{N}\right)^2.$$

The following observations furnish data for the determination of the absorbing powers of different glasses employed in the course of studies relative to the radiations from incandescent mantles.

ABSORBING GLASS PLACED BEFORE THE SOURCE TO BE STUDIED.

Temperature.	Aperture of cat's-eye.		
	Red.	Green.	Blue.
1270° (+ 1 glass)	19.5	21.2	35
1270 (no glass)	5.5	7.9	11.1
	$k_r = 12.5$	$k_g = 7.2$	$k_b = 9.9$

ABSORBING GLASS PLACED BEFORE THE STANDARD LAMP.

1170° (− 1 glass)	2.9	5.95	10.2
1170 (no glass)	9.4	16.1	31.5
	$k_r = 10.5$	$k_g = 7.3$	$k_b = 9.5$

Emissive Power. — Before being able to establish the relation which exists between the intensity of radiation of incandescent bodies and their temperature, it is necessary to know the emissive powers of these bodies (see page 293). For this measurement use was made by Le Chatelier of the principle stated above, — that the interior of fissures in bodies may be considered as inclosed in an envelope at uniform temperature. The emissive power is thus, at the temperature considered, equal to the ratio of the luminous intensity of the surface to that of the bottom of deep fissures, with the condition, evidently, that the aperture of the fissures be sufficiently small.

The body to be studied was placed in the state of a paste, as dry as possible, on the end of a couple previously flattened so as to take the form of a disk of 2 or 3 mm. diameter. The drying was very slow, so as not to have any swelling of the mass, and one obtained in this way a coating possessing fissures; the conditions described above are then satisfied. The end of the couple thus prepared is heated either in a Bunsen flame or a blast lamp, and the temperature of the junction is noted, while, simultaneously, readings are taken with the optical pyrometer. In order to obtain a temperature as constant as possible, it is necessary to guard against currents of air and use a flame of small size.

Here are some results obtained:

I. COUPLE COVERED WITH A MIXTURE CONTAINING 99 PARTS OF THORIUM AND 1 OF CERIUM.

	Red.		Green.		Blue.	
Temperatures.	(1)	(2)	(1)	(2)	(1)	(2)
950° (− 1 glass)	16.0	...	21.0	14.0	23.0	....
1170	15.5	9.0	11.0	9.0	12.0	12.0
1375	7.0	3.0	4.5	3.2	3.5	3.5
1525	3.2	2.0	2.0	2.0	1.9	1.9
1650 (+ 1 glass)	8.3	6.0	5.0	....	4.0	....

II. MAGNESIA.

	Red.		Green.		Blue.	
Temperatures.	(1)	(2)	(1)	(2)	(1)	(2)
1340° (−1 glass)	12.2	4.0	18.5	6.7	19.0	9.0
1460 (−1 glass)	4.9	2.5	8.2	3.1	7.7	4.1
1540 (−1 glass)	2.4	1.3	3.1	1.8	3.2	2.1

The numbers give the divisions of the cat's-eye; those of column (1) refer to the surface, and those of column (2) to the bottom of the fissures. The indications (− 1 glass) and (+ 1 glass) mean that the absorbing glass is placed either before the standard lamp or before the source studied.

Measurements of Intensity.—The following table gives an idea of the order of magnitude of the intensities of different luminous sources, the measurements of brightness being made in the red. Unity is the brightness of the axial portion of stearine-candle flame.

Carbon beginning to glow (600°)	0.0001
Silver melting (960°)	0.015
Stearine candle Gas flame Acetate of amyl lamp	1.0
Pigeon lamp, with mineral oil	1.1
Argand burner, with chimney	1.9
Auer burner	2.05
Fe_3O melting (1350°)	2.25
Palladium melting	4.8
Platinum melting	15.0
Incandescent lamp	40
Crater of electric arc	10,000
Sun at midday	90,000

Calibration. — Le Chatelier made a first graduation of his optical pyrometer by measuring the brightness of iron oxide heated on the junction of a thermoelectric couple, and admitting that, for the red, the emissive power of this substance is equal to unity. He found a law of variation of the intensity of the red radiations as function of the temperature, which is well represented by the formula

$$I = 10^{6.7} \cdot T^{-\frac{3210}{T}},$$

in which unit intensity corresponds to the most brilliant axial region of the flame of a candle. (T is absolute temperature.)

This formula has been shown by Rasch to be equivalent to (B), page 294, for red light, in which $\alpha = 13.02$. It is therefore a derivative from Wien's law (page 251).

The table below gives, for intervals of 100°, the intensities of red radiations emitted by bodies of an emissive power equal to unity. These numbers were calculated by means of the interpolation formula given above.

Intensities.	Temperatures.	Intensities.	Temperatures.
0.00008	600°	39	1800°
.00073	700	60	1900
.0046	800	93	2000
.020	900	1800	3000
.078	1000	9,700	4000
.24	1100	28,000	5000
.64	1200	56,000	6000
1.63	1300	100,000	7000
3.35	1400	150,000	8000
6.7	1500	224,000	9000
12.9	1600	305,000	10,000
22.4	1700		

These results are represented graphically in Fig. 111.

After having determined the value of the diaphragm opening d_0, which gives equality of brightness of the standard candle with that of the comparison lamp, and the absorbing power k of the tinted glasses, one may, as was said before, prepare a table which gives directly the temperature corresponding to each aperture of the cat's-eye.

With an apparatus for which

$$d_0 = 5.2, \quad k = \tfrac{1}{11},$$

the following table is obtained, in which the plus sign refers to tinted glasses placed before the objective, and the minus sign to those before the comparison lamp.

This graduation applies to all bodies placed in an inclosure at

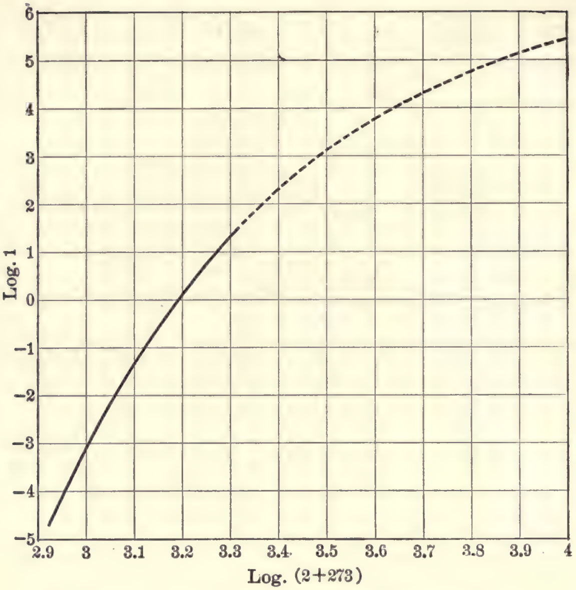

Fig. 111. Intensities in Terms of Temperatures.

the same temperature, — in the interior of furnaces for example, —and to black bodies whatever the temperature surrounding them; for example, it applies very closely for a piece of red-hot iron exposed to the free air. For bodies whose emissive power is inferior to unity, as platinum, magnesia, lime, it is necessary, when they are exposed to the air and not surrounded by an inclosure at the same temperature, to make a special calibration.

TYPICAL CALIBRATION TABLE FOR A LE CHATELIER OPTICAL PYROMETER.

	Aperture of the Cat's-eye.				
Temperatures.	−2 glasses.	−1 glass.	0 glass.	+1 glass.	+2 glasses.
700°	17·3	....	....	....	....
800	6.9	23.0	...	....	....
900	....	11.0	....	....	....
1000	....	5·6	18.6	....	....
1100	....	....	10.5	....	....
1200	....	....	6.5	....	....
1300	....	....	4.0	13·6	....
1400	....	....	....	9·4	....
1500	....	....	....	6.6	....
1600	....	....	....	4.8	....
1700	....	....	....	3·6	12.0
1800	....	....	....	....	9·1
1900	....	....	....	....	7·3
2000	....	....	....	....	5·9

Le Chatelier and Boudouard made a series of measurements on radiations of different wave lengths. The junction of a thermoelectric couple was placed in a small platinum tube, to realize approximately an inclosed space. By taking as unity the brightness of melting platinum, the results obtained are the following for the red, green, and blue radiations:

TEMPERATURE VS. BRIGHTNESS (IN TERMS OF MELTING PLATINUM).

t	Log $(t+273)$	I_r	Log I_r	I_g	Log I_g	I_b	Log I_b
900°	3.0707	0.0009	$\bar{4}.95$	0.00018	$\bar{4}.25$	0.00002	$\bar{5}.3$
1180	3.161	.0024	$\bar{3}.88$	.0087	$\bar{3}.94$	.0015	$\bar{3}.17$
1275	3.190	.075	$\bar{2}.78$	.037	$\bar{2}.57$	.013	$\bar{2}.11$
1430	3.230	.23	$\bar{1}.36$	.16	$\bar{1}.67$	.058	$\bar{2}.76$
1565	3.265	.72	$\bar{1}.86$	.47	$\bar{1}.20$	.24	$\bar{1}.38$
1715	3.300	1.69	0.23	1.45	0.16	.9	0.95

Evaluation of Temperatures. — Finally, Le Chatelier has used his optical pyrometer to determine the very highest temperatures realized in some of the most important phenomena in nature and in the industries. These results, quite different from previous determinations, were at first regarded with considerable reserve; they are admitted to-day as reasonable, at least within the limits of precision, and in terms of the temperature scale used by him. Here are some of the figures obtained:

Siemens-Martin furnace	1490° to 1580° C.
Furnace of glass works	1375 to 1400
Furnace for hard porcelain	1370
Furnace for new porcelain	1250
Incandescent lamp	1800
Arc lamp	4100
Sun	7600

This determination of the temperature of the sun, generally believed to be low at the time it was found, was confirmed by the experiments of Wilson and Gray (page 271) by a totally different method. Later determinations of the sun's temperature, using the more recently established laws of radiation (Chapter VI), give values between 5500° and 6500°.

A series of measurements were made with the same apparatus in ironworks. Here are some results:

BLAST FURNACE SMELTING GRAY PIG.

Opening before the tuyère	1930° C.
Tapping the pig iron, beginning	1400
Tapping the pig iron, end	1520

BESSEMER CONVERTER.

Pouring the slag	1580°
Pouring the steel into the ladle	1640
Pouring the steel into the molds	1580
Reheating of the ingot	1200
End of the hammering	1080

SIEMENS-MARTIN FURNACE.

Flow of the steel into the ladle, beginning	1580°
Flow of the steel into the ladle, end	1420
Flow into the molds	1490

Calibration in Terms of Wien's Law. — As approximately monochromatic radiation is used, the Le Chatelier optical pyrometer may be calibrated in terms of Wien's law (III) (page 251) by sighting upon a black body (Fig. 86) whose temperature is given by means of a thermocouple. For this purpose Wien's law may be written:

$$\log I = K_1 - K_2 \frac{1}{T},$$

where I is the intensity of light, in terms of the center of the Hefner flame for example, and T is the absolute temperature. This method of graduation has the advantage that only two points are required to completely calibrate the instrument, for the relation between $\log I$ and $\frac{1}{T}$ is linear, so that these quantities being plotted give a straight line which may evidently be extended to lower and higher temperatures, since Wien's law has been shown (page 250) to hold over the widest temperature interval measurable, provided the light used is monochromatic and the bodies observed approximate blackness and are not luminescent, that is, their light not produced by chemical or electrical excitation. The value of I is given by the equation of page 300, and for a given absorption glass and focus is proportional to d^2.

Precision and Sources of Error. — We shall give in some detail a discussion of the factors which in the use of the Le Chatelier optical pyrometer may influence the photometric settings and so affect the accuracy of temperature determinations, as results of such a discussion are illustrative of what may be expected from optical pyrometers in general. The results are taken from those of Waidner and Burgess, who have made an experimental comparison of all the available optical pyrometers.

The sources of error of this instrument may be those due to the standard Hefner amyl-acetate or other standard of constant photometric intensity or temperature placed before the cat's-eye when adjusting the pyrometer, the oil comparison lamp, the focusing system, the nature of the red glass used, and the coefficients of absorption of the tinted glasses. The first of these affects only comparative results with different instruments, while the others, if they exist, may be of considerable importance in work with a single instrument. We shall consider them in the order named.

As only the central portion of the amyl-acetate flame is used, variations in height and fluctuations in total intensity due to various causes such as moisture and carbonic acid in the atmosphere and changes due to differing samples of acetate become almost, if not quite, insignificant in this method of comparison; so that, when using only a small central area of the amyl-acetate flame, it is a very perfectly reproducible standard under the most varying conditions of burning. Again, the effects of any slight fluctuations in light intensity are further greatly reduced when transformed into temperature changes, as has been shown (page 238). Thus, the effect of varying the height of the Hefner flame by 1 mm., which amounts to 10 per cent of the total intensity when the whole flame is used, causes a change of less than 1 per cent in the intensity of light from the central area, which is equivalent to less than 0.5° C. change in temperature at 1000° C.

Although used intermittently as above indicated, the Hefner serves well enough as an ultimate standard by means of which the indications of all photometer pyrometers may be reduced to a common basis, yet the Hefner is not suited for use as comparison lamp in the pyrometer itself, as has been previously stated.

In a study of the constancy of the comparison lamp the following arrangement was adopted: In order to obtain a perfectly constant source of light with which to compare the flame, a 32-c.p. incandescent electric lamp was placed in a fixed position before the objective of the pyrometer and a glass diffusing screen inserted before the objective. The voltage across the lamp terminals was kept rigorously constant, thus giving an arbitrary but invariable standard of illumination.

The concordance of results obtained by different observers setting the gasoline flame and observing is shown below:

WITHOUT ABSORPTION GLASS.

Observer	1	2	3	4
Cat's-eye scale readings	7·4	7·8	7·6	7·3
	7·4	7·9	7·8	7·0
	7·2	7·7	7·6	8·0
	7·8	7·8	7·7	7·1
	7·7	7·7	7·8	8·3
	7·8	7·7	7·4	8·0
Means	7·55	7·73	7·65	7·60

Observers Nos. 2 and 4 had no previous experience in the use of the instrument.

WITH ABSORPTION GLASS.

Observer	1	3
Cat's-eye scale readings	25.7	25.8
	24.0	24.8
	23.6	26.0
	24.1	25.8
	25.4	24.8
	24.8	24.9
	24.8	25.3
Means	24.63	25.34

Here the greatest variation corresponds to less than 3 degrees in temperature at 1000° C.

To control accurately the flame height in the gasoline lamp, a sight was inserted consisting of a horizontal scratch 2 mm. above the window before the flame, and a very fine platinum wire in the same horizontal plane but in a collar behind the flame. With this improvement an observer can set and control the flame height to 0.2 mm. Such provision, however, is not necessary except in the most refined work, for experiment showed that for most purposes changes of over 2 mm. may be made in the flame height with unimportant changes resulting in the temperature estimation.

Considering the time effect of burning upon the flame height and intensity due to local heating and change of depth of oil, it was found that the flame ceases creeping up after ten minutes and will then remain at constant height to within 0.5 mm. until the oil is used up, in three hours; and during all this period the brightness of the flame does not change by an amount corresponding to more than 5 degrees in temperature.

It might be expected that oils of different grades would give widely differing results, but an examination of this possible source of error showed that different samples of gasoline and gasolines mixed with several per cent of a heavy kerosene gave identical results. This is of great importance in the practical use of the instrument, as it shows that a calibration made with a given sample of gasoline remains good for any other gasoline.

From the above it is clear that variations in brightness of the comparison flame due to all possible causes need not produce errors in temperature measurement of over 5° C. at 1000° C., that is, within the experimental limits of making the photometric setting.

Considering now the sources of error due to focusing and sighting upon the object whose temperature is sought, it is first to be noticed that there is a minimum distance from the object at which the pyrometer can be focused, this distance being somewhat over a meter, depending, of course, upon the focal length of the objective and length of drawtube. There is also a minimum area which can be sighted upon and give an image of sufficient size to completely cover the desired photometric field; this minimum size of object is about 6 mm. on a side when the instrument is at its least distance; for greater distances a larger area must be viewed.

The drawtube can easily be set to 2 mm. when focusing, and as the image is over 20 cm. from the objective in all cases, the resulting error in intensity due to focusing is not greater than 2 per cent. This corresponds to 1° C. in temperature, showing that an error of even 5 mm. in focusing the drawtube will not produce an appreciable error in temperature estimation.

Often, in use, the distance of the instrument from the objects studied needs to be changed considerably, and in rapid work it is not always convenient to refocus; a change in this distance of a fourth of its value, i.e., from 120 cm. to 150 cm., will produce an apparent change in intensity of only 9 per cent, or about 5° C. in temperature. That these errors of focusing are so small when interpreted into temperatures, showing that no unusual precautions are needed, is evidently of great convenience in the use of the instrument.

The nonmonochromatism of the red glass in the eyepiece produces no considerable error in temperature measurement up to 1600° C., although if this glass is not very nearly monochromatic the differences in hue in the two adjacent photometric fields — from the comparison lamp and other sources — are very troublesome, and the strain on the eye in matching them is considerable. For the best work at high temperatures a better glass than is usually furnished with the instrument must be used (see page 335).

There remains to be considered the error introduced due to uncertainty in the knowledge of the coefficient of absorption of the absorbing glasses. If an observation (N') is taken with, and then one (N) without, an absorption glass, we have

$$k = \left(\frac{N'}{N}\right)^2,$$

so that the accuracy in determining k depends directly upon the precision of setting and reading the cat's-eye opening. Errors of over 5° at 1000° C. can hardly occur from this cause, although the determination of k is the most difficult and uncertain of all the operations in optical pyrometry.

Modifications of the Le Chatelier Pyrometer. — For use in technical works and other places where there are sure to be strong drafts of air causing unsteadiness of the flame of the oil comparison lamp, the Le Chatelier pyrometer might be improved by the substitution of an electric incandescent lamp of low voltage (six) placed before a uniformly ground diffusing glass screen, which, illuminated by the incandescent lamp, becomes the constant-comparison source. The electric lamp may be mounted in a vertical arm which serves at the same time as a handle, and then the instrument becomes nearly as portable as an opera glass. The reliability of such a method of producing a comparison light of invariable intensity will be discussed when describing the Wanner instrument. Other modifications will be discussed under the Féry and Wanner optical pyrometers.

The Shore Pyroscope. — In this instrument (Figs. 112, 112 A) the principle used is similar to that of the Le Chatelier optical pyrometer, the parts being arranged in a slightly different manner. The temperature is read directly off a scale controlled by the diaphragm; the telescope is movable about a horizontal axis, and the lenses are protected by easily removable cover glasses. In taking an observation, the diaphragm is turned until the object sighted upon and the flame, viewed by reflection, are of the same brightness.

Féry Absorption Pyrometer. — This is similar to Le Chatelier's instrument, except that a pair of absorbing-glass wedges p, p' replaces the iris diaphragm; and the 45° mirror G, with parallel faces. is silvered over a narrow vertical strip, giving a photometric field of form shown at ab, when looking at a hot crucible. The instrument also has a fixed angular aperture, so that no correction has to be made for focusing or for varying distance from furnace. The comparison light L plays the same rôle as in Le Chatelier's pyrometer, and the range of the instrument may be similarly extended by the use of auxiliary absorbing glasses A, A'. Féry has in addition made his instrument movable about a horizontal axis, which is a convenience in sighting.

The *calibration* is equally simple. If x is the thickness of the

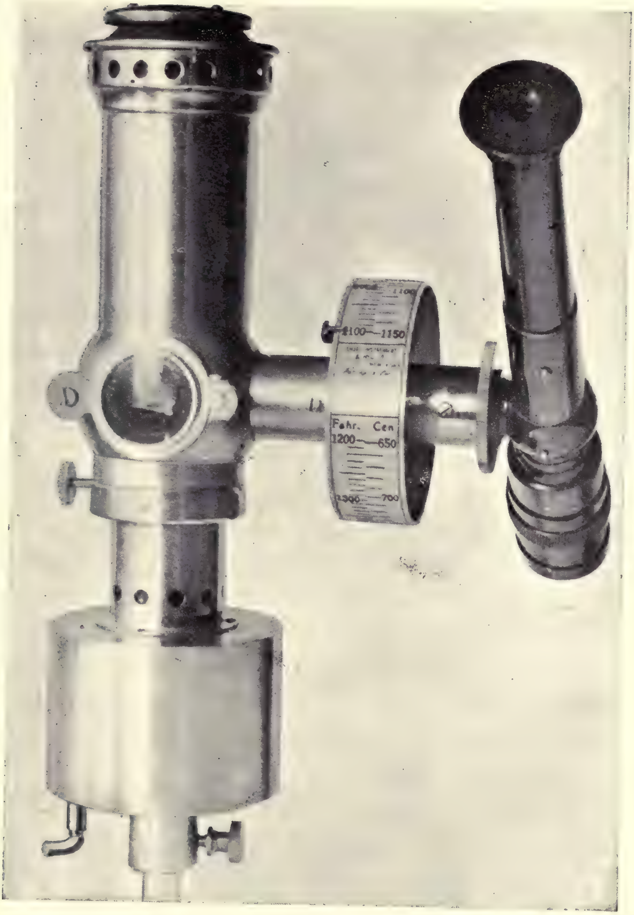

Fig. 112. Shore Pyroscope.

wedges, read off on a scale, when the light from the comparison lamp and furnace is of the same brightness, then the relation between brightness I and thickness of wedge is

$$I = c\epsilon^{kx},$$

where k is the coefficient of absorption of the glass of the wedges for the red light used and c is a constant.

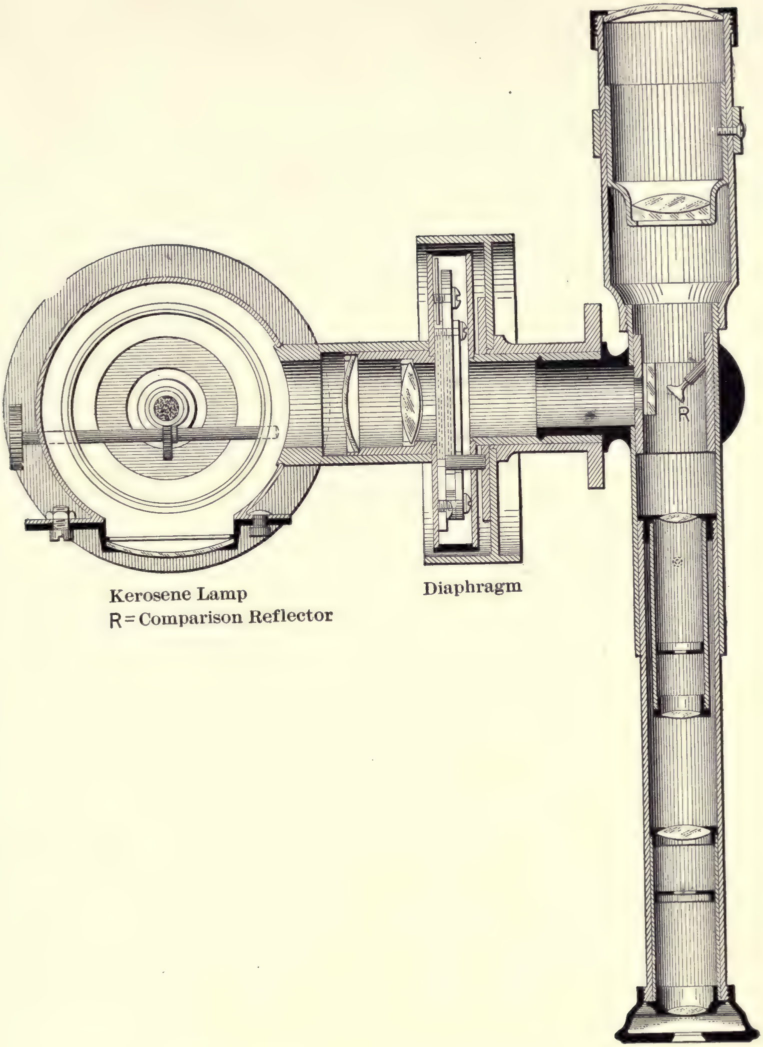

Fig. 112 A. Shore Pyroscope, Section.

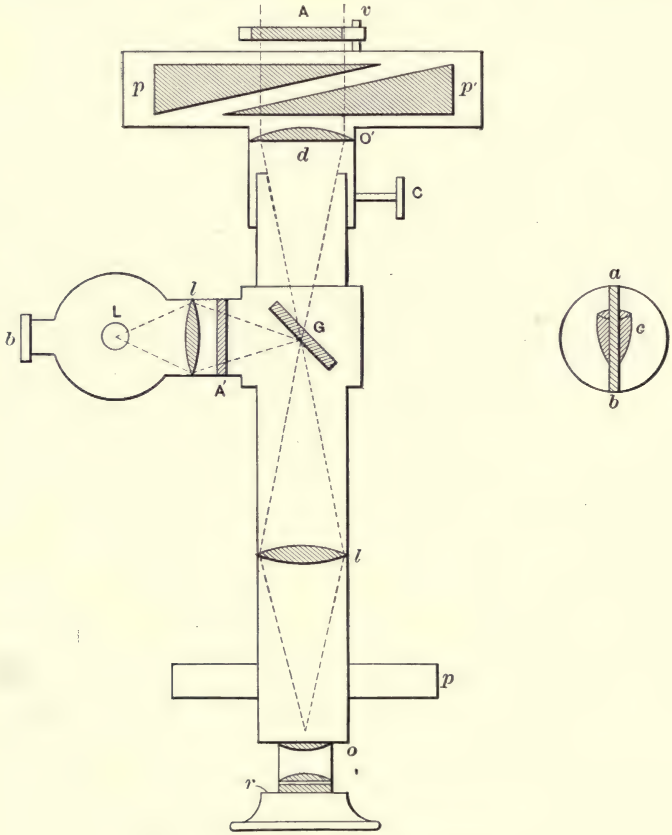

Fig. 113. Féry Absorption Pyrometer.

But by Wien's law III (page 251), assuming it to apply here,

$$I = A\epsilon^{-\frac{B}{T}},$$

or combining these two equations we have

$$c\epsilon^{kx} = A\epsilon^{-\frac{B}{T}},$$

whence

$$kx + C = \frac{-B}{T}\cdot$$

Thus it follows that the thickness of the wedge is inversely proportional to the absolute temperature, so that the calibration may be effected by finding the thickness of wedge for two temperatures only and plotting a straight line and constructing a table giving I and T respectively in terms of x.

It is questionable if there is any gain in substituting the wedge for the cat's-eye in the desire to extend the range over which the instrument may be used without employing the auxiliary absorbing glasses, for thereby the sensibility is somewhat reduced, and, more important still, the wedge instrument cannot be used at such low temperatures as the original Le Chatelier form, nor is there any gain in simplicity of calibration and ease of manipulation. The shape of the photometric field, the use of an aperture of constant angle, and making the instrument movable about a horizontal axis, however, are improvements over the Le Chatelier instrument; and the Féry instrument enjoys the further advantages that it may more conveniently be sighted on small objects, and fewer absorption glasses are needed.

Wanner Pyrometer. — Wanner, making use of the polarizing principle discarded by Le Chatelier, has brought out a photometer pyrometer which is a modification, suited to temperature measurements, of König's spectrophotometer.

The comparison light is a 6-volt incandescent lamp, illuminating a glass matt surface; monochromatic red light is produced by means of a direct-vision spectroscope and screen cutting out all but a narrow band in the red, and the photometric comparison is made by adjusting to equal brightness both halves of the photometric field by means of a polarizing arrangement.

The slit S_1 is illuminated by light from the comparison source, a small 4-volt electric lamp (Fig. 115), not shown in the Fig. 114, reaching S_1 after diffuse reflection from a right-angled prism placed before S_1. Light from the object whose temperature is sought enters the slit S_2. The two beams are rendered parallel by the lens L_1, and each dispersed into a continuous spectrum by the direct-vision prism P. Each of these beams is next separated by a Rochon prism R into two beams, polarized in planes at right angles. Considering only the red light, there would now be four images formed by the lens L_2 and distributed about the slit S_4. In order to bring two red images oppositely polarized exactly before this slit, a bi-prism B is interposed whose angle is such as to effect this for two images only, at the same time increasing the number of images to eight. There is now in the field of view before the Nicol analyzer, A, two contiguous red fields composed of light oppositely polarized, the light of one coming from S_1 alone, and of the other from S_2 alone. All the other images are cut off from the slit S_4. If the analyzer is at an angle of 45° with the plane of polarization of each beam, and if the illumination of S_1 and S_2 is of the same brightness, the eye will see a single red circular field of uniform brightness. If one slit receives more light than the other, one-half of the field will brighten, and the two may be brought to equality again by turning the analyzer carrying a graduated scale, which may be calibrated in terms of temperature.

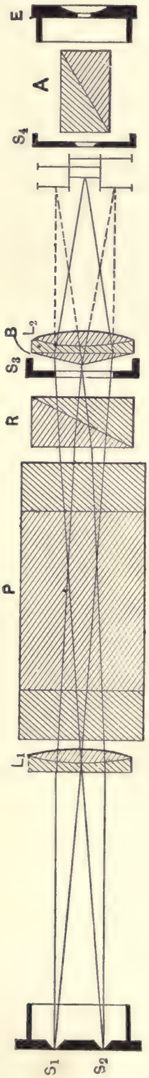

Fig. 114. Wanner Pyrometer, Section.

If the analyzer is turned through an angle ϕ to bring the two halves of the field to the same brightness, the relation between the two intensities from S_1 and S_2 is

$$\frac{I_1}{I_2} = \tan^2 \phi.$$

Calibration.— Since monochromatic light is used, and the comparison beam and that from the object examined undergo the same optical changes, Wien's law III may form the basis of the calibration.

As constructed and generally used, the 45° position of the analyzer when setting on the standard corresponds most conveniently to some intermediate arbitrarily chosen position on the graduated scale (Fig. 115) of the instrument. This reference position or "normal point" is the scale reading to which the instrument must be adjusted, by varying the current through the comparison lamp or its distance from the slit S_1, when sighting upon the standard amyl-acetate flame. The positions of the flame and pyrometer are fixed mechanically (see Fig. 115). The flame height must be carefully adjusted and the lamp should burn some ten minutes before standardizing.

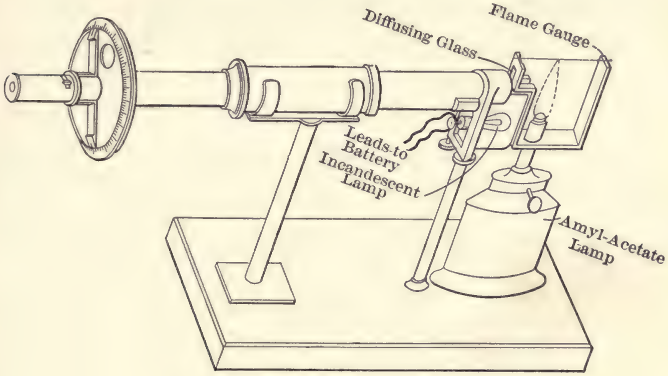

Fig. 115. Wanner Pyrometer.

If I_0 is the intensity of light from the standard amyl-acetate lamp, T_0 the corresponding equivalent temperature absolute, and ϕ_0 the reading in degrees on the scale of the instrument for the "normal point," and I, T, and ϕ are the intensity, apparent temperature, and scale readings when sighting upon the object whose temperature is sought, we have

$$\frac{I_0}{I} = \frac{\tan^2 \phi_0}{\tan^2 \phi}, \quad \ldots \ldots \quad (a)$$

assuming the circle to be uniformly graduated and the optical parts in adjustment. Also Wien's law III (page 251) gives us

$$\log_{10} \frac{I_0}{I} = \frac{c_2 \log \epsilon}{\lambda}\left(\frac{1}{T} - \frac{1}{T_0}\right). \quad \ldots \ldots \quad (b)$$

Since the constant $c_2 = 14,500$ for a black body and $\lambda = 0.656\ \mu$ as the instrument is usually constructed, a knowledge of the apparent black-body temperature of the standard source, together with the reading of the analyzer scale at the normal point when $I = I_0$, for such an instrument, is all the data required for its calibration, as any temperature may then be calculated by means of equations (*a*) and (*b*) in terms of the scale readings. The apparent temperature T_0 of the amyl acetate may be taken as 1673° abs. or 1400° C. This instrument may also, of course, be empirically calibrated in terms of the readings of a thermocouple, using a black body to sight upon (see p. 241).

The actual computation involved in a calibration is very simple, and is readily done graphically in a manner similar to that suggested for the Le Chatelier optical pyrometer. From equations (*a*) and (*b*) above we have

$$\log \tan \phi = a + b \cdot \frac{1}{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

so that if log tan ϕ is plotted in terms of $\frac{1}{T}$, we have a straight line of which b is the tangent and a the intercept on the log tan ϕ axis. If a and b are known for the type of pyrometer used, a single calibration temperature suffices, otherwise two observations of T and ϕ are required to completely solve (*c*). It is safer, however, to take several temperatures and draw the line best representing the observations according to (*c*). A table or a curve of ϕ *vs* t $(= T - 273)$ may then be constructed for practical use.

It is evidently necessary to be able to always reproduce exactly the standard intensity I_0. Now, the brightness of an electric lamp will vary with the current through it, so it is necessary to check frequently the constancy of illumination of the slit S_1 against a standard source of light. The amyl-acetate lamp and ground-glass diffusing screen are placed before the slit S_2, thus reproducing the standard light required. The analyzer is then set at the previously determined normal point and the distance of the electric lamp from S_1 adjusted or the current through the lamp changed by a rheostat, until the two fields appear of the same brightness.

In the latest form of this instrument the details of its mechanical construction have been improved, and it has been made direct-reading by providing a second scale on the instrument graduated in temperatures, corresponding, of course, to a definite normal point and for a source approximating a black body.

The amyl-acetate standardizing lamp may be eliminated wholly or in part in the use and calibration of the Wanner pyrometer. If the electric comparison lamp be fixed in position, the reading of the instrument sighted on a black body at a single temperature, as the gold point (adjusting the scale to a conveniently located "normal point"), or better, at a series of known temperatures, may be taken, for a definite current through the comparison lamp. If this same current is always maintained in the use of the instrument, this calibration will hold as long as the lamp does not change nor the optical parts of instrument become deranged. This last method of use is preferable in exact work where calibrating apparatus is available. The normal point, however, may still be that given by the amyl acetate if so desired. Or, the amyl-acetate standard with its corresponding normal point may be retained, but used only occasionally for checking and adjusting the constancy of the pyrometer, whose uniformity of indications is maintained in the meantime by keeping the current constant in the comparison lamp when taking measurements, and keeping the comparison lamp in a fixed position.

According to Nernst and Wartenberg, it may also be necessary to correct the circle readings by a constant fraction; thus they found that for a certain Wanner instrument the ratio $\frac{\tan^2 \phi_1}{\tan^2 \phi_2}$, taken over the scale by means of a sector disk, was not constant, but that the expression $\frac{\tan^2 m\phi_1}{\tan^2 m\phi_2}$ was constant, where m is nearly unity.

Sources of Error. — A study of a Wanner instrument by Waidner and Burgess has led them to the following conclusions. The sensibility of this pyrometer varies with change in the angle, and is so adjusted as to be the greatest between 1000° and 1500° C., and is about as follows:

0.1 scale div. ≎ 1° C. at 1000° C.
0.1 scale div. ≎ 2° C. at 1500° C.
0.1 scale div. ≎ 7° C. at 1800° C.

The reproducibility of the brightness of the amyl-acetate flame as viewed through the ground-glass diffusing screen is a measure of the ability of the instrument to repeat its indications. It is very important that this diffusing screen be always placed in exactly the same position relative to the flame and slit S_2, and further, that it be free from dust and finger marks. These requirements can only be satisfactorily met by protecting this screen by a cover glass and providing an adjustment for setting it exactly in place between the flame and slit.

The constancy of the amyl-acetate flame as used with this pyrometer under ordinary conditions of burning is illustrated by the following set of observations, during which the current through the electric comparison lamp was kept rigorously constant by means of a milliammeter and rheostat:

Reading of instrument.	Deviations.
39.9	−0.28
39.9	−0.28
40.1	−0.48
39.9	−0.28
39.1	+0.52
39.2	+0.42
39.8	−0.18
39.0	+0.62
39.6	0.38

This shows that the flame can be relied upon to give an intensity of illumination whose constancy expressed in terms of temperature is 0.5 per cent. Variations in height of the flame, if they do not exceed 2 to 3 mm., together with fluctuations in atmospheric conditions, will not produce errors in temperature estimation exceeding 1 per cent.

The uncertainty of setting the Nicol, due to lack of sensitiveness of the eye to exactly match the two halves of the photometric field, is also about 1 per cent, or slightly better with practice.

The adjustment of the electric lamp to standard intensity at the point on the scale chosen as normal point can be made, when proper care is taken regarding the diffusing screen, to 1 per cent expressed in temperature change. This source of error does not affect relative results in any one series for one setting to the normal point.

The most serious source of error, except when special precautions are taken, is the variation in brightness of the electric comparison lamp due to variation in the current furnished by the three-cell storage battery.

With the 10-ampere-hour battery furnished with the Wanner instrument, after making circuit the electromotive force drops by about 2 per cent in two minutes and then falls off slowly, but nearly recovers the original voltage after remaining on open circuit even for a very short time. When the battery is in good condition the variation in three hours at normal discharge (0.75 ampere) is about 0.08 volt, and somewhat less for the current (0.55 ampere) taken by the lamp; with the battery in poor condition these changes are much accentuated.

The following table illustrates the effect of slight variations in current through the lamp on apparent temperature of the amyl-acetate flame, for the small battery of 10 ampere hours furnished with the instrument. The apparent change in temperature is calculated from the current change:

SMALL BATTERY.

Time. Minutes.	Wanner scale.	Current in amperes.	Per cent change in current.	Apparent change in temperature.
15	31.2	0.5645	....	....
20	31.8	0.5640	0.1	1° C.
27	32.7	0.5550	1.7	10
37	34.6	0.5400	4.3	25
36	Disconnected battery two minutes.			
40	32.5	0.5610	0.6	3
42	31.7	0.5570	1.5	7
45	32.5	0.5560	2.5	15
47	33.1	0.5505	4.1	24

A battery of 75 ampere hours gave similar results.

The above results give abundant evidence of the need of maintaining the current through the lamp quite constant in work of precision. A series of experiments has shown that in the range 1000° to 1500° C. one division on the Wanner scale corresponds to about 0.009 ampere, or 1° C. apparent change in temperature is produced by a fluctuation of 0.0012 ampere through the lamp; hence to obtain a precision of 5° the current must be kept constant to 0.01 of its value. The above table shows that this is by no means effected by using the battery without regulating the current, for even with the battery in the best condition the current increases by 2 per cent in the first eight or nine minutes of discharge and then falls off 1 per cent in the next twenty minutes. The temperature coefficient of the battery would produce only insignificant changes. The table shows further that breaking the circuit and then making it again may cause an apparent temperature change of over 20° C. For work of precision, therefore, it is essential to keep the current constant by means of a milliammeter and rheostat, otherwise uncertainties of over 25° C. will occur in the temperature measurements. These will increase with the battery in poor condition.

Range and Limitations. — The above description of the Wanner pyrometer has shown the great loss of light due to the optical system employed. This prevents measuring temperatures below about 900° C. (1650° F.) with this instrument. There is no method of sighting this pyrometer exactly upon the spot desired, except by trial, as no image of the object examined is formed in the eyepiece, but this inconvenience is in part compensated by not having to focus with varying distance from the object.

There is another limitation which may in certain cases become a serious source of error: light from incandescent surfaces is, in general, polarized, and, as the Wanner instrument is a polarizing pyrometer, care must be taken to eliminate this source of error when it exists.

If an incandescent object is viewed normally, the amount of polarized light is very small, but, as the angle of incidence increases, the proportion of light polarized becomes greater and greater. Besides varying with the angle of incidence, the amount of polarized light emitted varies widely with different substances, being greatest for polished platinum and very much less for iron, glass, etc. In some measurements made with the Wanner pyrometer on the temperature of an incandescent platinum strip in the neighborhood of 1350° C., Waidner and Burgess have found a maximum difference in the readings of 90° C. for positions of the instrument at right angles to one another in azimuth and for an angle of incidence of 70° with the normal to the surface. This introduces, under these conditions, the possibility of an error of 45° C. in the temperature measurement. This source of error can be eliminated by taking the mean of four readings for azimuths 90° apart. The magnitude of the error arising from this cause is entirely negligible for all practical purposes for many substances, such as iron, porcelain, etc. A considerable area is needed to sight upon with this pyrometer, which is a disadvantage when small objects are viewed from a distance.

Due to the relatively large surface required in sighting the Wanner pyrometer, there is a tendency to bring the instrument too close to the furnace or object viewed, and this practice carried to excess may readily damage the instrument, deranging its optical parts and altering the calibration by very considerable amounts. Warning of overheating is sometimes given by the change in color of the field. Placing a water jacket between the furnace and instrument or otherwise screening the latter will evidently obviate this difficulty.

Where an attempt is made to sight on very small or distant areas, such as wires or narrow strips which fill only a small part of the photometric field, there may be produced diffraction effects, as noticed by Hartmann.

A review of the sources of error and limitations of the Wanner pyrometer shows that they may exert a relatively great effect on the temperature measurements, and it was, therefore, thought worth while to emphasize them; but, on the other hand, they may all be practically eliminated with reasonable care, and the instrument then becomes one of great precision and convenience, for those measurements for which it is adapted. We shall see later how its range may be extended to the highest temperatures.

Instrument for Low Temperatures. — In order to render his pyrometer available for temperatures below 900°, Wanner has brought out a modification suitable for use from 625° to 1000°, with two ranges, 625° to 800° and 800° to 1000° C., which gives a very open scale and renders the instrument available for a great many industrial operations that were hitherto inaccessible to it. In this low-temperature form, shown in Fig. 116, the light from the furnace does not pass through the polarizing system, and the direct-vision prism is replaced by a red glass in the eyepiece, by which elimination light of much feebler intensity than with the high-range apparatus can be observed. The apparatus is very compact and easy to manipulate. It requires as accessories a 4-volt storage battery, milliammeter, and amyl-acetate standard.

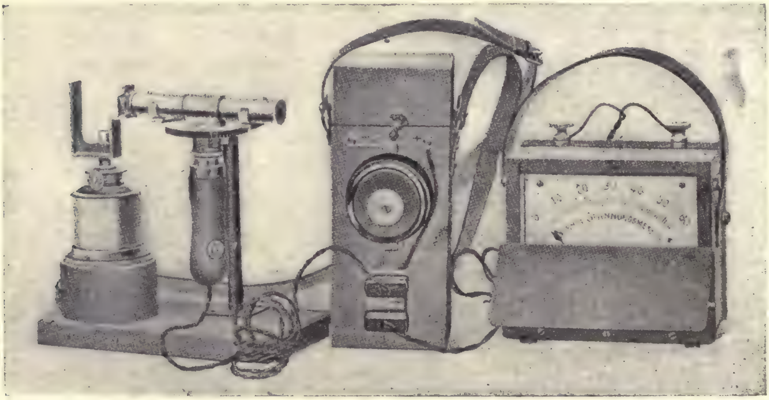

Fig. 116. Wanner Outfit for Low Temperatures.

Holborn-Kurlbaum and Morse Pyrometers. — If a sufficient current is sent through the filament of an electric lamp, the filament glows red at first, and as the current is increased the filament, getting hotter and hotter, becomes orange, yellow, and white, just as any progressively heated body. If now this filament is interposed between the eye and an incandescent object, the current through the lamp may be adjusted until a portion of the filament is of the same color and brightness as the object. When this occurs this part of the filament becomes invisible against the bright background, and the current then becomes a measure of the temperature as given either by a thermocouple or in terms of the intensity of illumination. This principle appears to have been first used by Morse and independently developed by Holborn and Kurlbaum. An absolute match of both color and brightness cannot be made unless monochromatic light is used or unless the lamp filament and viewed object radiate similarly.

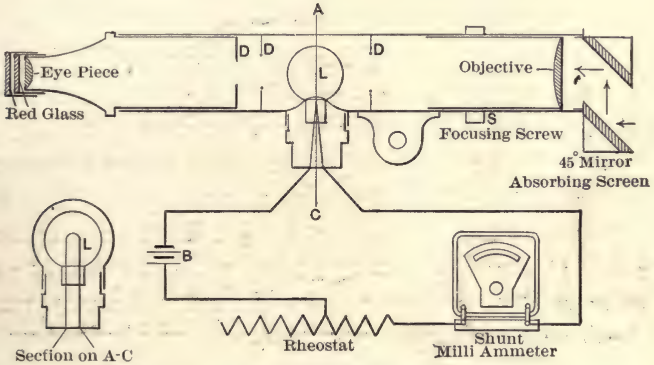

Fig. 117. Holborn-Kurlbaum Pyrometer.

Holborn-Kurlbaum Form. — A small 4-volt electric incandescent lamp *L* with a horseshoe filament is mounted in the focal plane of the objective and of the eyepiece of a telescope provided with suitable stops *D*, *D*, *D*, and a focusing screw *S* for the objective. The lamp circuit is completed through a two-cell storage battery *B*, a rheostat, and a milliammeter.

The determination of a temperature consists in focusing the instrument upon the incandescent object, thus bringing its image into the plane *AC*, and adjusting the current by means of the rheostat until the tip of the lamp filament disappears against the bright background, when a previous calibration of current, in terms of temperature for the particular lamp used, gives the temperature by reading the milliammeter.

As the temperature of the filament increases, the effect of irradiation or too great brightness becomes blinding, and the photometric comparison is then rendered possible at these temperatures by the introduction of one or more monochromatic red glasses before the eyepiece, giving as well all the advantages of photometry of a single color. Below 800° C. the measurements are more easily made without any red glass, as the filament itself is then red, and the lowest temperatures are, of course, reached with the least interposition possible of absorbing media. The lower limit of the instrument is very nearly 600° C. Two red glasses are required for temperatures above 1200° C., and for very high temperatures, above 1500° or 1600° C., it is necessary, in order to avoid overheating the lamp filament by the current, to put absorbing glasses or a double-prism mirror (Fig. 121) before the objective; and they also, of course, require calibration. At very high temperatures, unless a strictly monochromatic glass is used, the pyrometry becomes difficult, the filament never disappearing completely.

The eye is particularly sensitive in recognizing equality of brightness of two surfaces, one in front of the other, and this pyrometer, therefore, provides a very delicate means of judging temperatures, since the light intensity, as has been shown (page 238), varies so much faster than does the temperature.

The precision attainable with this pyrometer is illustrated by the following series of observations which are indicative of the ordinary performance of the instrument:

Temperature from H.-K. pyrometer.	Temperature from thermocouple.	Temperature from H.-K. pyrometer.	Temperature from thermocouple.
1347	1347° C.	632	634° C.
1351	1347	634	633
1343	1343	633	633
1333	1332	633	632
1342	1342		

Different observers do not differ by any appreciable amount in their readings, and at low temperatures the same values are obtained whether a red glass is used or not.

For the calibration of the instrument, it is necessary to find empirically the relation between the current through the lamp and the temperatures for a number of temperatures, and then interpolate either analytically, or more conveniently, graphically. The calibration will evidently be an independent one for each lamp used.

The relation between current and temperature is sufficiently well expressed by a quadratic formula of the form

$$C = a + bt + ct^2.$$

That this formula gives satisfactory results is shown by observations of Holborn and Kurlbaum for a lamp satisfying the equation

$$C\,10^3 = 170.0 + 0.1600\,t + 0.0001333\,t^2,$$

when sighted on a black body (page 239), the temperature of which is given by a thermoelectric pyrometer calibrated at known melting points.

C amp. 10^{-3}.	t obs.	t calc.	Δt.
340	686	679	−7° C.
375	778	778	0
402	844	850	+6
477	1026	1032	+6
552	1196	1196	0
631	1354	1354	0
712	1504	1504	0

We may also cite the behavior of one of the several standard pyrometer lamps of the Bureau of Standards. This lamp satisfies the equation

$$C = 0.1681 + 0.0_3\,1482\,t + 0.0_6\,1700\,t^2.$$

C in amps.	t obs.	t calc.	Δt
0.4486	920	921	−1°
.5305	1087.5	1087.5	0
.3357	650	649	+1
.6023	1221	1221	0
.3525	692	692.5	−0.5
.6393	1285	1285	0
.5309	1089	1088.5	+0.5

No appreciable change in the readings of this lamp could be detected over a five-year period, the lamp being used very frequently during that time to temperatures as high as 1500° C.

Pirani and Meyer have shown that, for carbon and metal filament lamps,

$$\log C = a + b \log T$$

where C = current and T = absolute temperature. This permits of a calibration with two temperatures only.

Mendenhall suggests that this pyrometer — and the same is true of all the optical instruments using monochromatic light — may be calibrated for all temperatures in terms of a single known temperature, such as the palladium melting point, by means of a series of sectored disks each of a different aperture, giving, by the application of Wien's law (see page 250), a corresponding series of effective temperatures. The sectors, of some 15 cm. diameter, may be rotated by means of a shaft attached to a small motor fixed near the middle of the outside of the pyrometer tube. Mendenhall has also made a direct-vision spectroscopic eyepiece for this instrument, and works with a field of about 25 A.U. width, giving λ to about one-fifth per cent in the middle of the visible spectrum.

Holborn and Kurlbaum as well as Waidner and Burgess have made a thorough study of the effects of aging.

Lamps which have not been aged or burned for some time at a temperature considerably above that at which they will ordinarily be used, undergo marked changes and are unreliable, but, if properly aged, they reach a steady condition, as indicated by the following table of results obtained by Holborn and Kurlbaum on these lamps. The current is given in each case for a temperature of 1100° C.

AGING OF LAMPS.

	Current.		
Lamp number	1	2	3
After 20 hours burning at 1900° C	0.608	0.592	0.589
After 5 hours burning at 1900° C	.613	.592	.592
After 5 hours burning at 1900° C	.621	.597	.597
After 5 hours burning at 1900° C	.622	.599	.600
After 20 hours burning at 1500° C	.622	.599	.601

If a lamp is not aged its indications may change by as much as 25° C. with time, but after twenty hours' heating at 1800° it will undergo no appreciable further changes over a period of time corresponding to many months if used in the shop, if not heated above 1500°. This state of permanence is sufficient to satisfy the most rigid requirements of practice.

By the substitution of tungsten for carbon filaments even greater permanence may be had, but the selective radiation of the metallic filament may then be a source of error or inconvenience in certain cases.

Morse Thermogage. — In its original form, instead of a simple horseshoe filament, Morse used a large spiral filament in the lamp of his pyrometer, so that in sighting upon an incandescent body it was necessary to choose some particular spot of the spiral and try to make that spot disappear. This is fatiguing, as the spiral covers a large area and is of just sufficiently varying intensity to cause the eye to wander. This effect was aggravated by the fact that this instrument was not a telescope, possessing no eyepiece or objective, so that the eye had to accommodate itself back and forth between the filament and the object studied.

Instead of the 4-volt battery for the Holborn-Kurlbaum lamps, the spiral lamp took a battery of 40 or 50 volts, requiring a costly installation unless the fluctuations of the ordinary 110-volt lighting circuit were not too troublesome to use it with a suitable rheostat or shunt.

The Morse instrument was designed for use in hardening steel, and, throughout the limited temperature range required in this process, in spite of the crudities of construction above noted, this pyrometer could be read to about 3° C. within this range. Above 1100° C., however, it is very difficult, and it soon becomes impossible to make a satisfactory setting.

Tests of these spiral filament lamps show that when aged at 1200° C. they will remain constant for several hundreds of hours within the range over which they are intended to be used.

It is interesting in this connection to note the behavior of ordinary carbon incandescent lamps as to permanence. (See Fig. 118.)

Later forms of the Morse thermogage are provided with lower voltage lamps with a single loop, red glass at the eyepiece, and made into a telescope, following, in part, suggestions given to Morse by Waidner and Burgess.

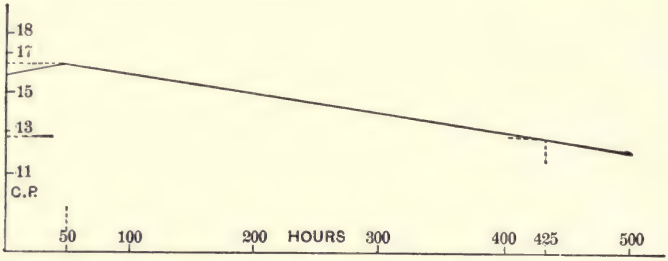

Fig. 118. Behavior of Carbon Lamp.

Henning's Spectral Pyrometer. — In order to eliminate the uncertainties and corrections for the lack of monochromatism of colored glasses used with the Holborn-Kurlbaum instrument, and to permit temperature measurements with any colored light, Henning has devised a spectral pyrometer suitable for exact work in the laboratory from 1000° C. It is essentially a combination of the Holborn-Kurlbaum instrument with a spectrometer as shown in Fig. 119. The collimator KL_2, telescope FL_1, carrying an observing slit D or an ocular, and Abbé prism P which can be set to give any wave length by means of the micrometer MNA, together with the slit E adjustable in width by

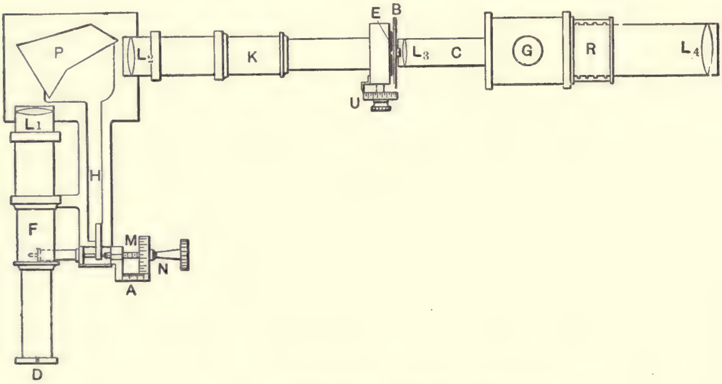

Fig. 119. Henning's Spectral Pyrometer.

the screw U, constitute the spectrometer. An image of the incandescent body is superposed on the lamp G by the lens L_4, and both are seen in colored light with the observer's eye before D. The screen B carries a series of suitable stops. The micrometer scale A is calibrated in wave lengths by means of light from standard sources, as helium and mercury vacuum tubes. The instrument may also be arranged for use as a spectrophotometer.

Henning has used his spectral pyrometer in a study of metal-filament lamps and for the determination of absorption and reflecting coefficients of metals. He has shown that, for a series of metals, the equation $\frac{1}{S} - \frac{1}{S_0} = \text{const.}$, in which S and S_0 are the absolute black-body temperatures for wave lengths λ and λ_0, holds over a wide range of temperatures; and that the absorption coefficients remain practically constant with change of temperature.

Calibration of Optical Pyrometers. — We have already called attention to the fact that the most accurate method of calibrating an optical pyrometer to about 1600° C. is to take its readings when sighted into an experimental black body (page 239) whose temperature is best given by two or more thermocouples which have in turn been calibrated by determining their E.M.F.'s at the freezing points of three or more pure metals. These calibrations are, in general, best left to a properly equipped standardizing laboratory. However, it is often desirable to be able to calibrate, at least approximately, one's own optical pyrometer, even if not in the possession of a complete standardizing equipment.

A fair substitute for the black body is a resistance-tube furnace of the Heræus type with a diaphragm, say a piece of graphite, inserted at its center, or a little back of this, and on which the optical pyrometer is sighted. The temperature of this diaphragm may be obtained with a calibrated thermocouple or optical pyrometer. Sighted into such a furnace, whose total length is some twenty or thirty times its diameter, an optical pyrometer will read some 5° to 15° C. too low.

The following method may also be used, and this requires no auxiliary pyrometer, but does require from one to three or more deep crucibles of substances of known melting points, preferably the pure metals, such as Al or Sb, Cu, Ni, or Fe. The optical pyrometer is sighted on the bottom of a porcelain tube, preferably blackened inside, and which is thrust into the melted metal, and the reading of the pyrometer taken at the freezing point of the metal.

Where several optical pyrometers are in use in the same establishment, it is well to have at least one of them calibrated carefully and kept as a standard. The others are readily calibrated by comparing their readings with that of the standard when sighted on any convenient incandescent source whatever, provided the pyrometers all use the same colored light; otherwise it is safer to use a furnace as source, although graphite or iron (oxide) will answer in most cases.

The criterium of a satisfactory comparison source for pyrometers using different colors is to view the source, when this is possible, with different colored glasses applied in succession to one pyrometer. If the same reading is obtained for all — red, yellow, and green, for example — the source is satisfactory.

The Wide-filament Comparison Lamp. — A very convenient and rapid method of standardizing one optical instrument in terms of another is shown in Fig. 120, which was devised by Waidner and Burgess for the determination of incandescent lamp filament temperatures and the melting points of very refractory metals. Fig. 120 illustrates the use of a carbon strip *C* mounted in vacuo for the former purpose. The standard pyrometer *L* and the lamp *F* whose filament temperature is sought are both brought to the same brightness as *C*, and the currents in *L* and *F* give a measure of their temperatures, which are assumed equal if the color of the glass *G* is the same as that used before *L* and if the filaments *F* and *L* are of the same material. The lenses *E* and *O* make the readings of *F* more convenient and equalize the two optical systems. Evidently any type of optical pyrometer may be substituted for the lamp *F* and calibrated in a similar manner.

These carbon-strip comparison lamps may be used intermittently to temperatures as high as 1800° C. or even 2000° C. If used only at comparatively low temperatures, they may themselves be calibrated in terms of current *vs.* temperature and then serve as a secondary standard, replacing the black body. Such lamps of this type as are at present available change pretty rapidly with even short burning, so that it is better to keep a filament lamp or other optical pyrometer as the standard and use the wide strips merely as comparison sources. For extending such comparisons to higher temperatures, it would be desirable to replace the carbon with tungsten strips, when probably 2500° C. or more could be realized.

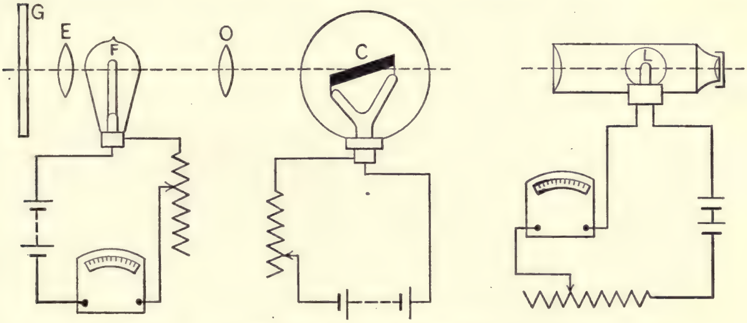

Fig. 120. Calibrating Method of Waidner and Burgess.

Other comparison sources are available, however, for these very high temperatures, such as the Arsem vacuum furnace (Fig. 176) with which temperatures of nearly 3000° C. may be attained, and, moreover, black-body conditions are completely realized.

Use of Wedge-shaped Cavities. — We have already seen that in the calibration of his optical pyrometer Le Chatelier took advantage of crevices in heated materials surrounding a thermocouple to obtain approximately black-body conditions. Féry has called attention to the necessity of the measuring instrument also being black in the Kirchhoff sense, at least when absolute measurements are made, and he developed the use of conical receivers.

Mendenhall, studying the relation between true and apparent temperatures of metals by means of the optical pyrometer, shows that if a thin metal strip is bent into a wedge of small angle, the radiation from within the wedge, heated electrically, as is a lamp filament, is very nearly that of a black body; so that simultaneous readings with a calibrated pyrometer on the outside and inside of such a wedge give a measure of the selective properties of its substance. The wedge may also replace the black body for the comparison of one optical pyrometer with another. Assuming specular reflection and the wedge angle L, the number of reflections perpendicular to the edge of the wedge is $n = \frac{180}{L}$; if the reflecting power of its material is r, that of the wedge is r^n. For many metals r is of the order of 0.7 for red light, when for a 10-degrees wedge $r^n = 0.0016$ and $e = a\epsilon = 0.998\ \epsilon$, corresponding to a temperature difference from a black body of the same brightness of only 0.5° C. at 1600°. For matt surfaces the departure from blackness is greater. The difference in temperature between the inner and outer surfaces of the wedge is less than 1° C. for metals of 0.04 mm. or less in thickness. By burning out such wedges of platinum, Mendenhall and Faryther obtained a value for the platinum melting point only 8 degrees lower than the figure of Waidner and Burgess (1753° C.).

Monochromatic Glasses. — In order to use Wien's law with exactness and convenience, and especially when extrapolation on the temperature scale is resorted to, it is highly desirable that there be no change in the color of the light used in an optical pyrometer. With those pyrometers in which the monochromatic light is produced by means of colored glasses, there may be an error introduced due to the lack of homogeneity of the light transmitted and to the consequent shift with temperature in the position of maximum intensity of the light. For such inhomogeneous glasses this is equivalent to introducing a continuous change of wave length with temperature in Wien's law (page 251).

The behavior of certain Jena glasses, which are among the best in the smallness of this effect, as found by Waidner and Burgess, is shown in the following table:

MONOCHROMATISM OF COLORED GLASSES (JENA).

Glass.	Thickness in mm.	Temperature of source (C).	λmax.	Limits of transmission band.
Red, No. 2745	3.04	1000	0.645μ	0.698μ–0.610μ
		1250	.650	.731 – .602
		1450	.656	.772 – .598
Red, No. 2745	6.05	1450	.661	.753 – .608
Green, No. 431$^{\mathrm{III}}$	6.18	1150	.547	.602 – .532
		1450	.546	.631 – .468
Blue, No. 3086	4.32	1320	.462	.500 – .421
		1470	.462	.511 – .408

The position of the optical center of gravity ($\lambda_{\text{max.}}$ in the table) is seen to remain stationary for the green and blue, but to shift slightly to longer wave lengths for the red glass, with increase in temperature. An error of 0.005μ in the estimation of the equivalent wave length for a colored glass corresponds to an error in temperature estimation of about 5° C. at 1750° C.

For some of the newer monochromatic Jena glasses the following data on the transmission coefficients have been issued by Schott and Genossen:

TRANSMISSION COEFFICIENTS (*D*) OF JENA GLASSES FOR 1 MM. THICKNESS.

Glass.		Fraction transmitted for wave lengths (in μ).					
Type.	Name.	λ=0.644	0.578	0.546	0.509	0.480	0.436
F 4512	Red filter	0.94	0.05	.....	.....	.....	.....
F 2745	Copper-ruby	0.72	0.39	0.47	0.47	0.45	0.43
F 4313	Yellow glass, dark	0.98	0.97	0.93	0.83	0.09	.....
F 4351	Yellow glass, medium	0.98	0.97	0.96	0.93	0.44	0.15
F 4937	Yellow glass, light	1.00	1.00	1.00	0.99	0.74	0.40
F 4930	Green filter	0.17	0.50	0.64	0.62	0.44	.....
F 3875	Blue filter	.....	.....	.....	0.18	0.50	0.73
F 3815	Neutral black	0.35*	0.35*	0.37*	0.35*	0.34*	0.30*

* For a thickness of 0.1 mm.

The fractional transmission D_x for any other glass thickness x_x is given by the expression $D_x = D^x$, where D is the transmission for 1 mm. as given in the table.

Extension of Scale. — All of the optical pyrometers based on the use of a single wave length, such as the Le Chatelier, Wanner, and Morse, may have their scales indefinitely extended by the use of neutral absorbing glasses (such as Jena Rauch Glas), reflecting mirrors, or prisms of black glass (see Fig. 121), or sectored disks, placed between the furnace, or other source whose temperature is to be measured, and the pyrometer.

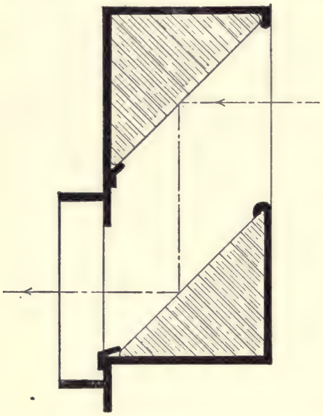
Fig. 121. Absorption Mirrors.

The same principle for the computing of temperatures with the screen in place applies for all of these screens and for any of these pyrometers. It is only necessary to find the *absorption coefficient* of the screen for the colored light used with the pyrometer. This absorption coefficient may be calculated by making use of Wien's law (page 251) and from observations at one or more temperatures. Thus, if K is the absorption factor, that is, the reciprocal of the absorption coefficient, T_1 and T_2 the apparent temperatures in degrees absolute given by the pyrometer, sighting on a black body first without and then with the absorbing screen, then Wien's law III gives

$$\log_{10} K = \log \frac{I_1}{I_2} = \frac{c_2 \log \epsilon}{\lambda} \left(\frac{1}{T_2} - \frac{1}{T_1} \right),$$

when $c_2 = 14{,}500$ for a black body, and λ is the wave length in μ (= 0.001 mm.) of the light used by the pyrometer. Applied to the high-range Wanner and Henning spectral pyrometers, the above formula applies exactly to the highest attainable temperatures if the absorbing screen has a constant coefficient for all brightnesses; but for those pyrometers using colored glasses, which are never strictly monochromatic, there will be an error entering into the extrapolations, which can, however, for the most part, be eliminated by the calibration in wave length *vs.* temperature of the colored glasses used, as shown in the preceding paragraph.

That these corrections can be made satisfactorily is shown by the following from the data of Waidner and Burgess on the determination of the melting point of platinum by means of a Holborn-Kurlbaum pyrometer using red, green, and blue glasses and provided with different kinds of absorbing screens. The metals were melted in an iridium-tube furnace approximating very closely a black body. The observations of Nernst and Wartenberg with a Wanner pyrometer using yellow light are also included, for comparison, their results being reduced to the same optical basis, i.e., for $c_2 = 14,500$ in Wien's formula. Measurements by the same observers on palladium gave equally concordant results.

ELIMINATION OF CORRECTIONS TO OPTICAL PYROMETERS.

Observers.	Absorbing screen.	Absorption factor.	Wave length.	Number of observations.	Melting point of platinum.
Waidner and Burgess....	Reflecting mirrors.........	199	0.668	23	1753° ± 3 C.
	Reflecting mirrors.........	228	0.547	7	1751 ± 3
	Sector disk......	35.4	0.668	10	1753 ± 2
	Sector disk......	35.4	0.547	6	1748 ± 2
	Sector disk......	35.4	0.462	4	1749 ± 3
Nernst and Wartenberg.	Rauch glass.....	147	0.5896	4	1750 ± 5

For most materials heretofore used as absorbing screens, either of the mirror or transmitting glass type, there is a rapid variation in absorbing factor with wave length of the incident light (see page 335 and above table). Schott and Genossen of Jena now furnish a "neutral black" glass (F 3815) of an absorbing factor which remains very constant throughout the visible spectrum. The fractional transmission for this glass is given in the table on page 333.

The use of a sector disk is preferable for exact work in the laboratory where the intensity of the source observed has to be cut down, for this form of screen has a constant absorption factor which may be determined geometrically with great exactness. The absorbing glasses are usually more convenient to use than the reflecting mirrors and are equally as good, or better.

Some Scientific Applications. — Our knowledge of phenomena occurring at very high temperatures has been increased greatly in the past few years, largely due to the availability of convenient and precise optical pyrometers using monochromatic light. We shall pass briefly in review some of the uses to which this type of instrument has been put in the laboratory as illustrations of what may be accomplished in high-temperature measurements by optical means.

Temperature of Flames. — Any substance inserted in a flame will take up a lower temperature than that of the flame itself, due to conduction, radiation, and diminished speed of the gas stream around the body. E. L. Nichols, by using thermocouples of progressively finer wires, sought to determine true flame temperatures by extrapolating for a wire of zero diameter. The uncertainty of this method is considerable, although it gives consistent results, which are probably low.

The radiation methods have been employed by several experimenters. The temperature as given by an optical pyrometer will depend on the thickness and density of the flame as well as upon its reflecting and absorbing powers. The reflecting power of a flame is small and probably varies with the kind of flame; the results as yet obtained are quite discordant on this point.

Kurlbaum interposed a flame between a black body and the eye and assumed that the two were of the same temperature when the flame disappeared against its background. This method gave results lower than those obtained by Lummer and Pringsheim (page 252). Kurlbaum and Stewart both claim that the carbon in the flame departs more widely from a black body than platinum, and the latter gets 2282 for the value of A in Wien's displacement equation $\lambda_m T = A$, assuming Nichols's value 1900° C. for the acetylene temperature. Féry has shown, however, that the brightness of the sodium line, measured with a spectrophotometer, is not increased by passing obliquely a beam from an electric light across the flame studied, seeming to indicate that the diffusing power is nil for the light coming from carbon. This would imply a value of A of the order of 2800, or of 2400° C. for the acetylene flame, assuming $\lambda_m = 1.05$.

Féry's method of measuring flame temperatures is to produce the reversal of a metallic line by means of light emitted by a solid body brought to the proper temperature. The image of the filament of an incandescent lamp is thrown by a large-aperture lens onto the narrow slit of a spectroscope. The rays from the filament pass through the flame to be studied, which contains sodium or other metallic vapor. When the filament is raised in temperature the D line, say, is ultimately reversed, and at the moment of disappearance the filament and flame are assumed to have the same temperature, which may be measured by sighting an optical pyrometer on the filament.

Some of Féry's results are as follows:

Bunsen	Open	1870° C.
	Half-open	1810
	Shut	1710
Acetylene		2550
Oxyhydrogen with illuminating gas and oxygen		2200
Oxyhydrogen with $H_2 + O$		2420

For this determination Féry used his absorption pyrometer. The results obtained may be slightly high, but hardly by more than 100° C., as a fine wire of platinum may be melted in an open Bunsen.

There have been other estimations of apparent temperatures of flames by various optical methods based on the radiation laws, some of which have given values greatly below the true temperatures, as measured by the ability of these flames to melt refractory materials of known melting point.

Making use of Wien's displacement law in form $\lambda_{\max} T = 2940$, Ladenburg found 1405° for the Hefner and 1842° for the acetylene flame. Becker, by a spectrophotometric method, obtained 1395° for the Hefner.

Kurlbaum and Schulze, by a method similar to Féry's, found apparent variations in Bunsen flame temperatures when colored with different salts; but E. Bauer, using the same method, showed that by using a definite part of the flame no such differences exist from one salt to another nor from one color to another. For the oxyhydrogen flame Bauer finds 2240° by applying Planck's law, and 2200° to 2300° by the reversal of the D line, using an electric arc as source of light in Féry's method. Bauer found from 1660° to 1850° for various portions of the Bunsen flame, using several optical methods.

All of the above methods assume that flames are nonluminescent, otherwise the results obtained are too high. Absurd results will also be obtained if the flames are colorless, i.e., contain no finely divided particles heated by the flame, as in an open Bunsen.

Temperature of Glow-lamp Filaments. — Since the observations of Le Chatelier with his optical pyrometer, and of Lummer and Pringsheim making use of the Wien relation $\lambda_m T = \text{const.}$, there have been numerous determinations of lamp temperatures by means of optical pyrometers. The first satisfactory observations for a series of lamps were made by Waidner and Burgess in 1906, using their graphite-strip method of comparison (page 330), and the Holborn-Kurlbaum instrument, furnished with red, green, and blue glasses in succession before the eyepiece to enable estimations of true temperature to be made from the apparent temperatures, which last, of course, depend upon the selective radiation of the filament surfaces. They found that for platinum filaments inclosed in an evacuated glass bulb, adding the difference in temperature between the blue and red readings to the apparent temperature with blue light when sighted on the carbon strip, there was given very nearly true temperatures — for example, 1760° C. for the platinum melting point.

Assuming this empirical relation to hold generally, they found the following:

NORMAL BURNING TEMPERATURES OF GLOW LAMPS.

Type of lamp.	Watts per candle power.	Volts.	Observed black-body temperatures (red).	Maximum true temperature.	Minimum true temperature.
Carbon........	4.0	50	1710° C.	1800° C.	1755° C.
Carbon........	3.5	118	1760	1850	1805
Carbon........	3.1	118	1860	1950	1905
Tantalum......	2.0	110	1865	2000	1935
Tungsten......	1.0	100	2135	2300	2215

In some of the other estimations no attempt has been made to correct for the lack of blackness of the filaments, and the results appear to be generally too low. We may cite the following determinations:

NORMAL LAMP TEMPERATURES BY VARIOUS OBSERVERS.

Observers.	Carbon.	Tantalum.	Tungsten.	Method and remarks.
Grau.......	1660	....	1850	Iridium strip and Wanner pyrometer.
Coblentz...	1785	1910	2060	$\lambda_m T = C$ and graphite "black."
	1570	1670	1810	$\lambda_m T = C$ and platinum "black." Temperature obs. of Waidner and Burgess with red light.
Féry.......	1780	....	1875	Combination of Wien and Stefan laws; assumes W behaves like Pt. Used absorption pyrometer.
Pirani......	....	2000	2080	Resistance and optical measurements.
Joly	1650 to 1720	1740	1810	Total photometric (Nernst); other methods gave lower values.

These figures are not strictly comparable, as the ratings are not exactly the same; roughly, they are $W = 1.25 \frac{W}{c.p.}$, $Ta = 1.5 \frac{W}{c.p.}$ and carbon $= 3.5 \frac{W}{c.p.}$.

The use of the equation $\lambda_m T = C$ (Coblentz) is questionable, as the form of the energy curves of lamp filaments is not that of the black body.

The normal burning temperature of the Nernst filament has been measured several times, ranging from the absurdly low result of Hartmann of 1535° obtained with a thermocouple, to the value 2360° of Ingersoll by a luminous-efficiency method. Mendenhall and Ingersoll found that rhodium would melt on a Nernst filament below its normal burning, and that iridium would not, which places this temperature at about 2100° C.; an application of Wien's law gave them 2125° C.

Temperatures within Furnaces. — The optical pyrometer, especially in its forms due to Wanner and to Holborn and Kurlbaum, has been of the greatest use in studying very high temperature phenomena, including the formation, modification, and dissociation of many chemical products. Besides the numerous melting-point determinations described elsewhere, we may mention as illustrations the work of Nernst and his associates at Berlin on gaseous dissociation to temperatures above 2000° C., carried out in his type of iridium furnace; of Tucker and others at Columbia University on carborundum and other furnace products; of Thompson at the Mass. Inst. of Technology on a series of chemical reactions; of Greenwood and of Prim at Manchester, using a carbon vacuum and pressure furnace, on boiling points of the metals and on the temperature of formation of many chemical substances. In all of the above investigations the Wanner pyrometer was used, but where the furnace opening is small, as is usually the case, there is advantage in using an instrument requiring only a few millimeters area to sight on, as the Holborn-Kurlbaum type. This has been used at the Reichsanstalt in comparing the optical and gas scales, and at the Bureau of Standards in most of the high-temperature work there, as well as at the Geophysical Laboratory. Using an Arsem furnace (Fig. 176), Dr. Kanolt with this pyrometer has been able to measure melting and freezing points of salts, alloys, and minerals to temperatures above 2100° C. by taking the heating and cooling curves and making use of the latent heat of transformation. A few tenths of a gram of material are sufficient to give a very sharp point (see Fig. 122).

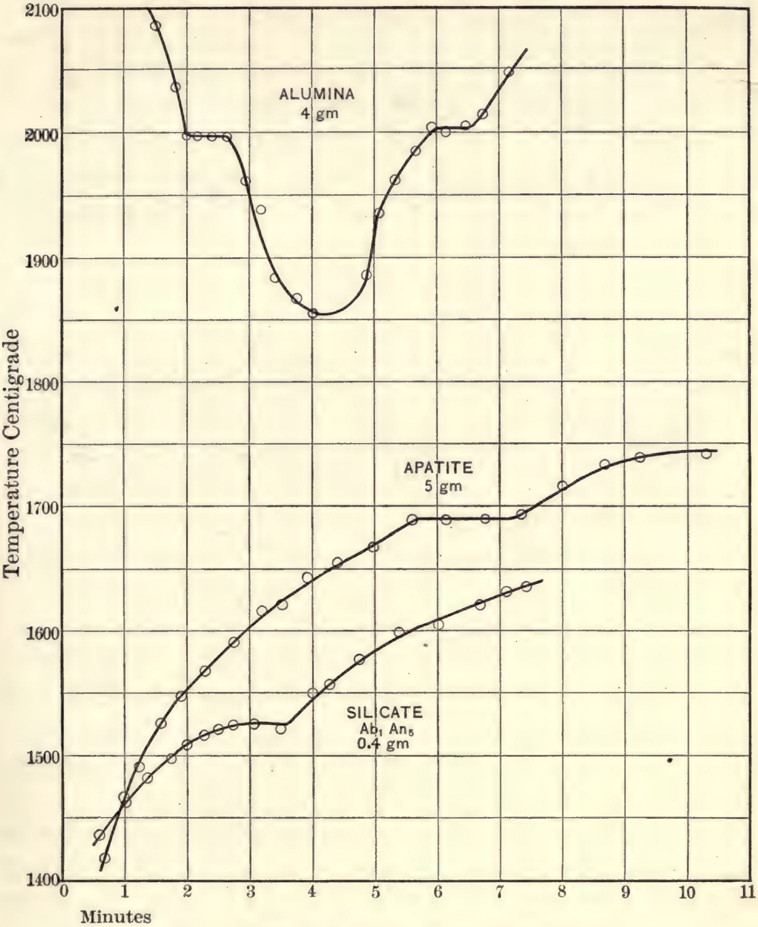

Fig. 122. Melting Points with Optical Pyrometer.

Melting points of microscopic samples may also be obtained readily with the Holborn-Kurlbaum pyrometer by making use of the known departure from blackness, or the emissivity, of some substance such as platinum, on a strip of which, or other suitable material such as iridium, carbon, or tungsten, may be placed the substance whose melting point is sought.

In Fig. 123 is shown the apparatus of Burgess used for the determination of the melting of points of the iron group (Chap. XI) in hydrogen, using samples of the order of 0.001 mg. melted on a platinum strip heated by a delicately adjustable electric current. The container is of brass blackened inside, and simultaneous observations are taken through a mica window of the melting of the sample with a microscope and of the temperature of the strip with the pyrometer.

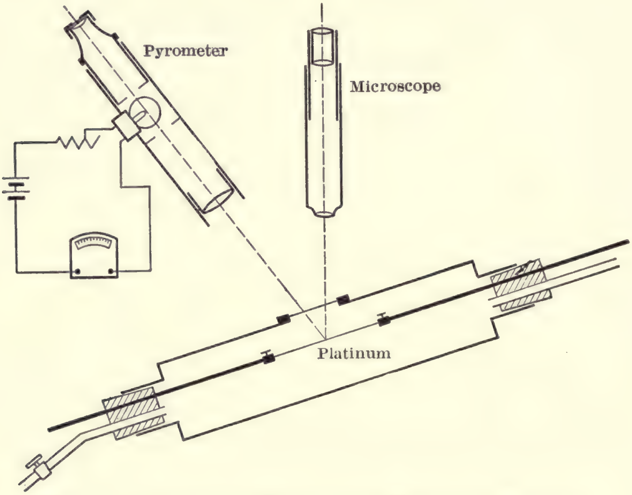

Fig. 123. Apparatus of Burgess for Microscopic Samples.

Conditions of Use. — The optical pyrometer using monochromatic light, by reason of the uncertainty of emissive powers and of the relatively slight sensibility of the eye for comparisons of luminous intensities, cannot give quite as accurate results as the electric methods, although the accuracy attainable, since the satisfactory establishment of the laws of radiation throughout practically the attainable temperature range, is sufficient, as we have seen, when proper precautions are taken, for all industrial and most scientific needs. The range of this pyrometer is from about 650° C. to the highest attainable temperature.

The optical or radiation pyrometer is peculiarly well adapted for many cases in which other methods fail, as when contact with the object whose temperature is sought cannot be made or when for any reason the pyrometer must be placed at a distance; for example, in the case of a moving body, as a rail passing into the rolling mill; in the case of very high temperatures, as of the crucible of the blast furnace or that of the electric furnace; in the case of isolated bodies radiating freely into the air, as flames or wires heated by an electric current which cannot be touched without changing their temperature. We have also seen that it may give very exact results in such cases when the emissive properties of the substances sighted upon are known, as is often the case.

It is also convenient in the case of strongly heated furnaces, as steel and porcelain furnaces. But in this usage care must be taken to guard against the brightness of the flames, always hotter than the furnace, and against the entry of cold air. The arrangement with the closed tube described in connection with the heat-radiation pyrometer is advisable if it is desired to obtain the most exact results. The optical pyrometer has the inconvenience to require active intervention on the part of the operator and can hardly be intrusted to a workman without oversight, while the set-up of the heat-radiation pyrometer may be made so that an observation reduces to a reading upon a scale. The latter pyrometer, however, is the more subject to error due to lack of blackness, flames, and furnace gases.

Some Industrial Uses. — The several forms of optical pyrometer using monochromatic light have been very generally introduced into industrial practice, where they are rendering most useful service, and for many operations they may advantageously replace the eye of the operator. Practically every furnace operation can be controlled by this type of pyrometer with great precision, with a resulting saving of fuel and a more uniform furnace product. A few of the types of furnaces for which such pyrometers are adapted are the various steel-melting furnaces, blast furnaces, coke ovens, ceramic kilns, and glass weirs. In forging, annealing, hardening, and similar operations on steel, and in foundry practice in general, such pyrometers are equally useful.

We have already called attention (page 305) to some industrial measurements made by Le Chatelier with his optical pyrometer. We may also mention some determinations with the Wanner pyrometer on a battery of six coke ovens:

Oven.	1	2	3	4	5	6
Over the retorts	1232	1264	1370	1464	1409	1436
Just over generator	1409	1397	1464	1397	1296	1264
Fifth flue	1126	1002	1112	1104	1096	1119
Next to last flue	992	982	918	932	970	932

The Morse or Holborn-Kurlbaum type may be sighted on distant objects conveniently. It is possible to set up such an instrument in a foundry or forging shop and from one position measure temperatures of several furnaces, of pieces under the hammer, and of metal being poured into and from ladles.

Measurement of the Relative Intensity of Different Radiations. — It is on this principle that rests the eye estimation of temperatures such as are made by workmen in industrial works. Numerous attempts, none very successful, have been made to modify this method and make it precise. There is need to consider this mainly from the point of view of a rough control over the heating of industrial furnaces. Recently a modification of this method has been devised by Nordmann, which, as we shall see, is of interest in the estimation of the extremely high temperatures of stars.

Use of the Eye. — Pouillet made a comparison of the colors of incandescent bodies in terms of the air thermometer. The table that he drew up is reproduced everywhere to-day:

POUILLET'S COLOR SCALE.

First visible red	525°	Dull orange	1100°
Dull red	700	Bright orange	1200
Turning to cherry	800	White	1300
Cherry proper	900	Brilliant white	1400
Bright cherry	1000	Dazzling white	1500

The estimation of these hues is very arbitrary and varies from one person to another; more than that, it varies for the same person with the exterior lighting. The hues are different by day from those by night; it is thus that the gas flame, yellow during the day, appears white at night. It is only in the reds that any accuracy can be had by the eye method. Workmen can sometimes guess to better than 25° C. up to 800° C. At 1200° errors of over 200° will be made.

Use of Cobalt Glass. — One may exaggerate the changes of hue in suppressing from the spectrum the central radiations, the yellow and green for example, so as only to keep the red and the blue. The relative variations of two hues are the greater the more separated they are in the spectrum; now, the red and the blue form the two extremities of the visible spectrum.

It has been proposed for this purpose to use cobalt glass, which cuts out the yellow and green, but lets pass the red and blue. It must be remembered that the ratio of the radiations transmitted varies with the thickness of the glass as well as with their absolute intensities.

Let I_a and I_b be the intensities of the radiations emitted, k_a and k_b the proportions transmitted by the glass through a thickness 1. Through a thickness e the proportion transmitted will be

$$\frac{I_a k_a^e}{I_b k_b},$$

which will vary with e in all cases that k_a is different from k_b.

It results from this that two cobalt glasses, differing in thickness or in amount of cobalt, will not give the same results. So that if the cobalt glass habitually used is broken, all the training of the eye goes for naught.

Besides, cobalt has the inconvenience of having an insufficient absorbing power for the red, which predominates at the more ordinary temperatures that we make use of. It would be possible, without doubt, by the addition of copper oxide, to augment the absorbing power for the red.

One would have better and more comparable results by employing solutions of metallic salts or of organic compounds suitably chosen. But few trials have been made in this matter.

Pyroscope of Mesuré and Nouel. — It is known that by placing between two nicols a plate of quartz cut perpendicularly to the axis, a certain number of the radiations of the spectrum are suppressed. This latter is then composed of dark bands whose spacing depends on the thickness of the quartz and the position of the angle of the nicols. Mesuré and Nouel have utilized this principle in order to cut out the central portions of the spectrum; this solution is excellent and preferable to the use of absorbing media. The apparatus (Fig. 124) consists essentially of a polarizer *P* and an analyzer *A*, whose adjustment to extinction gives the zero of graduation of the divided circle *CC*. This circle is graduated in degrees and is movable before a fixed index *I*. Between the two nicols *P* and *A* is a quartz *Q* of suitable thickness, carefully calibrated. The mounting *M* allows of its quick removal if it is necessary to verify the adjustment of the nicols *P* and *A*. The quartz *Q* is cut perpendicularly to the axis. A lens *L* views the opposite opening *C* furnished with a parallel-faced plate glass or, where desired, with a diffusing glass very slightly ground.

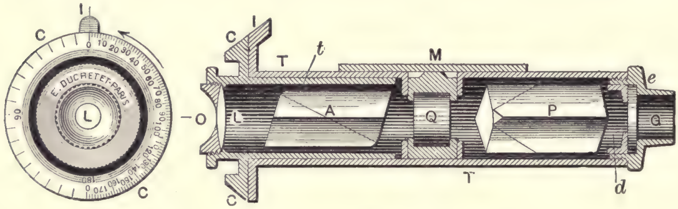

Fig. 124. Apparatus of Mesuré and Nouel.

The relative proportions of various rays that an incandescent body emits varying with the temperature, it follows that for a given position of the analyzer *A* the composite tint obtained is different for different temperatures.

If the analyzer is turned while a given luminous body is viewed, it is noticed that the variations of coloration are much more rapid for a certain position of the analyzer. A very slight rotation changes suddenly the color from red to green. Now, if the analyzer is left fixed, a slight variation in the temperature of the incandescent body produces the same effect. The transmission hue red-green constitutes what is called the sensitive hue. There are then two absorptions, one in the yellow and the other in the violet.

This apparatus may be employed in two different ways. First fix permanently the analyzer in a position which gives the sensitive hue for the temperature that is to be watched, and observe the changes of hue which are produced when the temperature varies in one direction or the other from the chosen temperature. This is the ordinary method of use of this instrument. It is desired in a given manufacturing process (steel, glass) to make sure that the temperature of the furnace rests always the same; the instrument is adjusted once for all for this temperature. It suffices to have but a short experience to train the eye to appreciate the direction of the change of hue.

The inventors have sought to make of their apparatus a measuring instrument; this idea is quite open to debate. In theory this is easy; it suffices, instead of having the analyzer fixed, to make it turn just to the securing of the sensitive hue and to note the angle which gives the position of the analyzer. But in fact the sensitive hue is not rigorously determinate and varies with the observer. A graduation made by one observer will not hold for another. It is not even certain that the same observer will choose always the same sensitive hue. At each temperature the sensitive hue is slightly different, and it is impossible to remember throughout the scale of temperatures the hues that were chosen on the day of the graduation. There is even considerable difficulty to recall this for a single temperature.

The following figures will give an idea of the differences which may exist between two observers as to the position of the sensitive hue:

	Temperature.	Angle of analyzer. (1)	(2)
Sun	6000°	84	86
Gas flame	1680	65	70
Red-hot platinum	800	40	45

The errors in the estimation of temperatures which result from the uncertainty of the sensitive hue will thus exceed 100°. With observers having had more experience the difference will be somewhat reduced, but it will remain always quite large.

Crova's Pyrometer. — Crova endeavored to give to the method of estimation of temperatures based on the unequal variation of different radiations of the spectrum a scientific precision by measuring the absolute intensity of each of the two radiations utilized; but this method, from the practical point of view, does not seem to have given more exact results than the preceding ones.

The eye is much less sensitive to difference of intensity than to difference of hue, so that there is no advantage in making use of observations of intensity.

Crova compared two radiations,

$$\lambda = 676 \text{ (red)},$$
$$\lambda = 523 \text{ (green)},$$

coming from the object studied and from the oil lamp used as standard. For this purpose, by means of a variable diaphragm, he brings to equality one of the two radiations emanating from each of the sources, and measures afterwards the ratio of the intensities of the two other radiations.

The apparatus is a spectrophotometer. Placed before half the height of the flame is a total reflecting prism, which reflects the light from a ground glass, lighted by the radiations from an oil lamp, having first passed through two nicols and a diaphragm of variable aperture. On the other half of the slit is projected by means of a lens the image of the body to be studied.

Before using the apparatus it is necessary to adjust the extreme limits of the displacement of the spectrum so as to project successively on the slit, in the focus of the eyepiece, the two radiations selected ($\lambda = 676$ and $\lambda = 523$). For this purpose there is interposed between the two crossed nicols a 4-mm. quartz plate which reëstablishes the illuminations; for extinction again, the analyzer must be turned 115° 38′ for $\lambda = 523$, and

$65° 52'$ for $\lambda = 676$. The instrument is then so adjusted that the dark band produced by the quartz is situated in the middle of the ocular slit.

The apparatus thus adjusted, in order to make a measurement at low temperatures, inferior to those of carbon burning in the standard lamp, one brings to equality the red radiations with the diaphragm, then, without touching the diaphragm again, the green is brought to equality by turning the nicol.

The optical degree is given by the formula

$$V = 1000 \cos^2 \alpha,$$

denoting by α the angle between the two principal sections of the nicols.

For higher temperatures the operation is reversed; one brings first the green to equality by means of the diaphragm, then the red to equality by a rotation of the analyzer. The optical degree is then given by the formula $N = \frac{1000}{\cos^2 \alpha}$, and the rotation varying from 0° to 90°, the optical degrees vary from 1000° to infinity.

This method, which is theoretically excellent, possesses certain practical disadvantages:

1. Lack of precision of the measurements. In admitting an error of 10 per cent in each one of the observations relative to the red and green radiations, the total possible error is 20 per cent; now, between 700° and 1500° the ratio of intensities varies from 1 to 5: this leads to a difference of $\frac{1}{25}$ in 800°, or 32°.

2. Complication and slowness of observations. It is difficult to focus exactly on the body or the point on the body that one wishes to study. The set-up and the taking of observations sometimes require about half an hour.

3. Absence of comparison in terms of the gas scale.

The *a priori* reason that had led to the study of this method was the supposition that, in general, the emissive power of substances was the same for all radiations and that consequently its influence would disappear by taking the ratio of the intensities of the two radiations. The measurements of emissive power given previously prove that this hypothesis is the more often inexact.

Crova also suggested that the upper limit of the spectrum of an incandescent body might be used as a measure of its temperature, and Hempel has tried this method with a special form of spectroscope, using a luminescent screen for observing when the upper spectrum limit is beyond the visible radiations; but, as compared with the photometric and radiation pyrometers, only crude results can be obtained.

Use of the Flicker Photometer. — Lummer and Pringsheim have shown that the combination of a spectral apparatus with a flicker photometer permits of greatly increasing the accuracy of the method of comparison of the intensities of two colors, and also permits the use of Wien's law (page 251) in the calculation of temperatures.

Sighting on a black body at the absolute temperature T, and measuring the two intensities I_1 and I_2 corresponding to the wave lengths λ_1 and λ_2, we have from Wien's law:

$$\log \frac{I_1}{I_2} = 5 \log \frac{\lambda_2}{\lambda_1} + \frac{c_2 \log \epsilon}{T} \left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right),$$

in which T is the only unknown. Thürmel has shown that the Purkinje effect does not vitiate the observations, and that results good to better than 2 per cent can be obtained, and that an observer will repeat his readings within this limit of error.

Here are some of Thürmel's observations on a black body:

TEMPERATURE WITH SPECTRAL FLICKER PHOTOMETER.

Ratio of wave lengths.	Temperature with— Optical apparatus.	Thermocouple.
660–480	1502°	1477°
660–500	1489	....
660–480	1742	1698
660–500	1703	....

Sighting on other objects than a black body will give incorrect temperatures, usually low, due to the difference in shape of the intensity curve from that of a black body, and on account of the varying value of the absorption coefficient with wave length from one substance to another (see page 256).

Stellar Pyrometers. — Of recent years there has been an increasing interest among astronomers in the determination of the physical characteristics of the stellar bodies, resulting in the development and modification of physical instruments suited to their needs. Assuming that the ratio of intensities of two spectral colors, red and blue for example, varies according to Planck's law (page 251) for the terrestrial and celestial bodies sighted upon, M. Nordmann has recently constructed a heterochrome photometer and used it for the estimation of effective stellar temperatures.

With this apparatus, which is still in a somewhat crude state of development, measurements are made, in the various parts of the spectrum, of the brightness of the star under observation referred to that of an artificial star realized by means of a secondary electric standard, interchanging, in the path of rays common to the two stars, a series of monochromatic liquid screens.

Consider measurements with red and blue light.

If T, T', T'', . . . are known temperatures of definite light sources, given, for example, by electric furnaces and the carbon arc, and if R, R', R'', . . . and B, B', B'', . . . are the corresponding intensities of the images as measured through red- and blue-light filters respectively by means of the stellar photometer, then, according to Planck's law, the relation $\log \frac{R}{B}$ *vs.* $\frac{1}{T}$ is a straight line. With the apparatus once standardized at known temperatures therefore, it is only necessary to measure the red and blue intensities for any light source as a star, in order to find its apparent or black-body temperature. The temperature found will approach the true temperature the more nearly the spectral-energy curve of the star approaches that of the black body. In the form of apparatus used by Nordmann, it is also necessary to correct for the shift of equivalent wave length with temperature of the monochromatic screens used. This could be avoided by transforming the apparatus into a spectrophotometer in much the same manner as Henning's spectral pyrometer eliminates the colored glasses of the Holborn-Kurlbaum instrument.

Some of the results found by M. Nordmann for effective stellar temperatures absolute are as follows:

ρ Persei	2870°	Polaris	8,200°
ζ Cephii	4260	α Lyræ	12,200
Sun	5320	δ Persei	18,500
γ Cygni	5620	λ Tauri	40,000

M. Féry has realized a form of stellar pyrometer which eliminates the use of colored screens. The principle of this apparatus, which is based on Wien's displacement law (page 249), consists in modifying the color of a comparison lamp by changing the ratio of the monochromatic intensities which it emits, so as to match this color with that of the star whose temperature is to be measured.

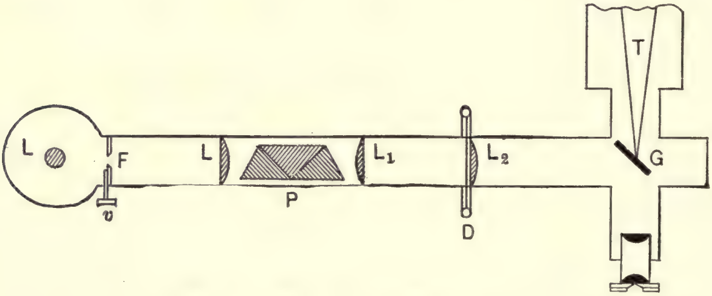

Fig. 125. Féry Spectral Pyrometer.

In order to realize this principle, the light from the lamp *L* (Fig. 125), after passing through the slit *F*, is dispersed by the direct-vision prism *P*, and, by means of the lenses *L* and L_1, forms a spectrum in the plane of a diaphragm *D*, to which we shall return. A third lens L_2 forms, on the half-silvered mirror *G*, a white or undispersed image of the face of the prism *P*.

The light from the star is concentrated by a telescope objective, whose tube is shown at *T*, and an image of the star is formed on the nonsilvered part of the mirror *G*, and may be examined by an ocular simultaneously with the adjacent luminous area due to light from the comparison lamp.

Fig. 126 gives the details of the diaphragm *D* of Fig. 125. The spectrum is formed between the two screens *V* and *V′*; this last is semicircular and may be turned about *A* as an axis. This rotation of *V′* causes the ratio of the intensities of the extreme red and blue rays to vary and gives to the field as projected by the lens L_2 (Fig. 125) the desired color.

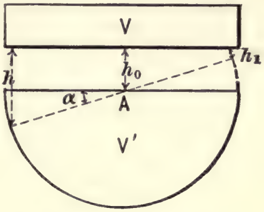

Fig. 126. Detail of Diaphragm.

Both of the above types of apparatus may be calibrated for the lower temperatures by means of an electric furnace, and for the higher stellar temperatures by taking the arc and sun temperatures as fixed points.

Spectrophotometric measurements of the apparent temperatures of the sun and 109 stars have been made by Wilsing and Scheiner, using as comparison source an incandescent lamp calibrated against a black body. Light of five wave lengths was used, and the observations were reduced in terms of Planck's law, using an equation similar to that of p. 255. Here are some of their results, assuming $c_2 = 14{,}600$.

WILSING AND SCHEINER'S STELLAR TEMPERATURES (ABS.).

Sun	5130 to 5600°	α Leoni	8700°
ζ Pegasi	7900	α Lyræ	8100
α Pegasi	8700	γ Geminorum	6900

We shall return to the question of the sun's apparent temperature in Chapter XI.

Action of Light on Selenium. — It has been known for a long time that light incident upon selenium changes the electric resistance of the latter, and pyrometers based on this principle have been devised. Light from an incandescent source whose temperature is sought falls upon a selenium cell forming part of an electric circuit in which are a battery and ammeter. As the light varies in intensity due to changes in temperature, the resistance of the selenium varies, and the indications of the ammeter may be empirically calibrated in terms of temperature. As selenium is quite insensible to the invisible heat waves, the lower limit of this method is above incandescence. Selenium also requires some time to recover its original resistance after being acted upon by light, and this lag might prove troublesome. As a dial instrument is used, the method could readily be made recording.

CHAPTER IX.

VARIOUS PYROMETRIC METHODS.

WHILE some of the several types of pyrometer which we have described in the preceding chapters have, by a process of elimination, become generally recognized as meeting most requirements for high-temperature measurements, scientific and industrial, there nevertheless remain several methods, some of which are useful in special fields of investigation or practice, and others mark some important development in the history of pyrometry. We shall mention briefly a few of these methods.

Wedgwood's contraction pyroscope, the oldest among such instruments, presents to-day hardly more than an historic interest, for its use has been almost entirely abandoned. It utilizes the permanent contraction assumed by clayey matters under the influence of high temperature. This contraction is variable with the chemical nature of the paste, the size of the grains, the compactness of the wet paste, the time of heating, etc. In order to have comparable results, it would be necessary to prepare *simultaneously, under the same conditions*, a great quantity of cylinders, whose calibration would be made in terms of the gas thermometer. Wedgwood employed cylinders of fire clay, baked until dehydrated, or to 600°; this preliminary baking is indispensable, if one wishes to avoid their flying to pieces when suddenly submitted to the action of fire. These cylinders have a plane face on which they rest in the measuring apparatus, so as always to face the same way (see the frontispiece). The contraction is measured by means of a gauge formed by two inclined edges; two similar gauges of 6 inches in length, one an extension of the other, are placed side by side; at one end they have a maximum separation of 0.5 inch, and at the other a minimum separation of 0.3 inch. Longitudinally the divisions are of 0.05 inch; each division equals $\frac{1}{240}$ of $\frac{2}{10}$ of an inch, or $\frac{1}{1200}$ inch, which corresponds to a relative contraction of $\frac{1}{1200} \div \frac{5}{10} = \frac{1}{600}$ in terms of the initial dimensions.

We then have the following relation between the Wedgwood degrees and the linear contraction per unit of length:

Wedgwood	0	30	60	90	120	150	180	210	240
Contraction	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40

Le Chatelier has made experiments to determine the degrees of the Wedgwood pyrometer in terms of the scale of the air thermometer by making use of clayey substances of different kinds, and in the first place of the cylinders from an old Wedgwood pyrometer of the École des Mines. The contraction which accompanies the dehydration is quite variable with the nature of the pastes. In these experiments the time of heating was half an hour.

Centigrade temperature	600°	800°	1000°	1200°	1400°	1550°
Wedgwood	0	4	15	36	90	132
Argile de Mussidan	0	2	14	36	78	120
Limoges porcelain	0	0	2	21	88	91
Faïence de Choisy-le-Roi	0	2	5	12	48	75
Faïence de Nevers	0	0	0	32	Melted	Melted
Kaolin	0	4	12	15	55	118
Clay 25 Titanic acid 75	0	4	9	19	123	160

This table shows how variable are the observations; it is impossible, consequently, to compare the old measurements of Wedgwood and of his successors, because the manufacture of the cylinders has varied with the course of time.

Wedgwood had given a graduation made by a process of extrapolation which he has not explained, — a graduation according to which he attributed 10,000° C. to 130° of his pyrometer, which corresponds to about 1550°. One might still seek to reëstablish the graduation by utilizing the determinations of the fusing points of the metals made by Wedgwood, but the results are too discordant to warrant any definite conclusion. According to Wedgwood, copper would be more fusible than silver, iron would not be far removed from silver; it is probable that these observations were made with very impure metals, or at any rate were made with metals much oxidized before their fusion. In any case the cylinders which he made use of in his first experiments assume a much greater contraction than those of the pyrometer of the School of Mines whose graduation was given above. One might with considerable reserve indicate the following graduation for measurements made with the first cylinders employed about the year 1780:

Wedgwood degrees.........	0	15	30	100	140
Centigrade degrees.........	600	800	1000	1200	1400

The preparation of the cylinders was a most care-taking operation. Molded in soft paste, they were necessarily somewhat irregular. After the first baking they had to be trimmed to bring them to a uniform size. To-day, in several pottery works where the method is still employed, a much greater regularity is obtained by using a very dry paste, 5 per cent of water for example, molding it under great pressure, about 100 kg. per square centimeter, in molds of turned steel. The precision of the measurements is increased by augmenting the diameter, to 50 mm. for example. It is necessary at the same time to reduce the thickness to about 5 mm., in order that the compression be uniform throughout the mass.

This apparatus cannot be recommended in any instance as a true pyrometer, serving indirectly to evaluate temperatures in terms of the air-thermometer scale. The graduation is laborious and can only be made by means of the intermediary of another pyrometer; the use of fixed points is not adapted for this graduation because the curve of contraction of clay in function of the temperature is too irregular for two or three points to determine it; in no case do the indications of this instrument possess any considerable precision.

But as simple pyroscope, that is to say, as an apparatus to indicate merely the equality or inequality of two temperatures, the Wedgwood pyrometer is very convenient. It has the advantage of costing almost nothing and it is easy to use and within the comprehension of any workman. It seems to be particularly recommendable for certain ceramic industries, in which the ordinary pastes found there may be used to make the contraction cylinders. It is necessary for this that the normal baking of these pastes be stopped at a temperature comprised within the period of rapid contraction. This is the case with fine faïence and with ordinary earthenware. That would not be the case, however, for stanniferous faïence nor for porcelain, because the baking of the first is stopped before the beginning of the contraction, and that of the second after its finish.

Expansion of Solids.—Some of the earliest forms of indicating pyrometers were based on the relative expansion of two metals, or of a metal and graphite or fire clay. Some of these instruments have had and still enjoy a very wide use both in Europe and America, often under the name *mechanical thermometers* for the lower-range instruments, and some of them are suitable for certain industrial processes not requiring exact temperature determination or control. A common form of dial instrument is shown in Fig. 127. A tube of iron incloses a rod of graphite, and their differential expansion with change in temperature is communicated by levers to a pointer turning over a dial graduated in degrees. The upper limit of these instruments is about 800° C. (1500° F.), but they deteriorate rapidly when used at the higher temperatures. Their indications change with time, due to changes produced in the materials by continued heatings. Correcting the zero of such an instrument, which should be done frequently, does not completely correct the rest of the scale, as the expansion properties of the two materials change differently with heating. Varying depths of immersion will also change the readings.

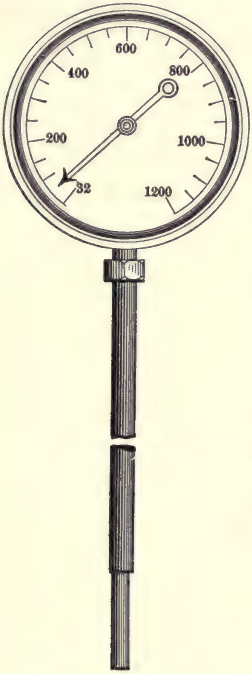

Fig. 127. Expansion Pyrometer.

The Joly Meldometer. — A modified form of this instrument was previously mentioned (page 271). As in its usual form it may be of great service to chemists, mineralogists, and others in determining the melting points and identification of minute specimens of minerals, salts, metals, and alloys, a further description may be of interest.

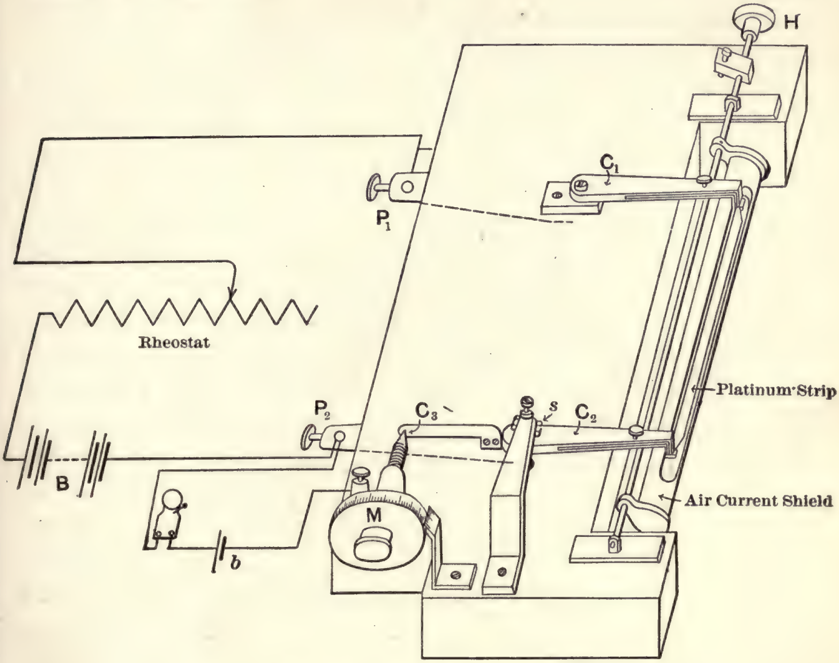

Fig. 128. Joly's Meldometer.

A platinum strip (Fig. 128) 10 cm. long, 4 mm. wide, and 0.02 mm. thick is held between two clamps *C*, *C*, and kept under a slight tension by the spring *s*. A storage-battery current controlled by a small step rheostat *R* is sent through the platinum strip whose length at any instant is given by the micrometer screw *M*, whose contact is made appreciable by the closing of the circuit of an electric bell. The platinum strip is calibrated preferably by means of salts of known melting points, as KNO_3 (399° C.), KBr (730°), NaCl (800°), and K_2SO_4 (1060°). Metals may also be used, but they tend to deteriorate the platinum. The upper limit of the instrument is about 1500° C., the Pd point being obtainable with difficulty. Permanent elongation sets in somewhat before this point is reached. The gold point (1063° C.) can be determined to 2° C., and only a few moments are required for an observation.

To take an observation, a speck of the specimen whose melting point is sought is placed on the middle of the strip under a low-power microscope magnifying about twenty-five times. The current is increased and at the instant of melting, as observed with the microscope, the micrometer is set to make contact and read; when by interpolation, most conveniently made graphically, the temperature is found corresponding to the length of strip observed. This instrument gives a nearly but not quite linear relation between length of strip and temperature.

High-range Mercury Thermometers. — Although mercury boils normally at about 356° C., yet this liquid subjected to high pressure may be kept from boiling and, suitably inclosed, may be used as thermometric substance to much higher temperatures. Compressed under an atmosphere of some inert gas, as nitrogen or carbonic acid, and inclosed in a very hard glass, the mercury thermometer can be used up to 550° C. (1000° F.). When a thermometer designed for only moderate temperatures, 200° C. or less, is sealed off gas free, there will be distillation of the mercury into the colder parts of the bore unless the column projects sufficiently above the heated region or the whole thermometer is immersed.

There are two methods of producing the necessary pressure within the bore to prevent distillation and boiling of the mercury. In the one, there is a small bulb at the top of the bore, and the thermometer is sealed off at atmospheric pressure with the mercury at ordinary temperature; in the other, there is a large upper bulb, and the sealing off is done at increased pressure, making use of an auxiliary bulb. The second construction is preferable, as the internal-pressure change with rise of temperature, and consequent deformation of the main bulb containing mercury, is much less than with the first.

Due to deformations in the glass, and consequent changes in readings, all high-range mercury thermometers should be furnished with some fixed point, preferably the ice point. This permits controlling conveniently the behavior of the thermometer due to changes in the volume of the bulb after the instrument has been calibrated. The bulbs of such thermometers should be carefully annealed, before filling, at a temperature higher than the instrument is to be used, and the thermometer should also be annealed after it is made and allowed to cool slowly, otherwise considerable and irregular changes in its indications will occur, amounting to several degrees. It is also advantageous to heat and cool slowly the thermometer a great many times before testing and using it. The zero reading of such a thermometer should be taken after every observation in work of precision. If a considerable length of stem emerges into the air when taking a reading, a very considerable error, 25° C. or so, may be introduced at high temperatures due to the difference in temperature of the bulb and stem. This "stem correction" varies slightly from one kind of glass to another and is very nearly:

$$\begin{aligned}\text{Stem correction} &= 0.00016 \cdot n \cdot (T - t)^\circ \text{ C.},\\ &= 0.000088 \cdot n \cdot (T - t)^\circ \text{ F.},\end{aligned}$$

where n = number of degrees emergent from bath;
T = temperature of bath;
t = mean temperature of the emergent mercury column determined by some auxiliary means, as the *faden* thermometer of Mahlke.

Among the thermometric glasses for the construction of high-range instruments, and the upper limits to which they may be used safely, are: Jena 16^{III} normal, Corning normal, and the French *verre dur*, which reach 450° C. or somewhat higher; Jena 59^{III}, a borosilicate glass, although sometimes graduated to 550° C., should not be used over 520° C.; with special grades of combustion tubing 570° C. may be reached. If after proper annealing and preliminary heat treatment the zero of a thermometer falls, it is being used at too high temperatures.

Thermometers which are to be used as high-temperature primary standards, or instruments which reproduce in themselves the temperature scale, should have both the ice and steam points, which permits calibrating the instrument in terms of the fundamental interval 0° to 100° C. Due to the fact that the mercury-in-glass expansion varies from glass to glass, and is also different for all of them from the gas expansion on which the temperature scale is based, it is necessary to apply a correction to reduce the readings of a mercury-in-glass thermometer to the gas scale, unless the thermometer was originally "pointed" in terms of this scale. The relation between the scales given by Jena glasses and the gas scale is shown in the following table:

VARIATION FROM GAS SCALE OF JENA-GLASS THERMOMETERS.

Gas scale.	Jena 16^{III}	Gas scale.	Jena 59^{III}
0	0	0	0
100	100.00	100	100.0
150	149.90	200	200.7
200	200.04	300	304.1
220	220.21	325	330.9
240	240.46	350	358.1
260	260.83	375	385.4
280	281.33	400	412.3
300	301.96	425	440.7
		450	469.1
		475	498.0
		500	527.8

If the bore of the thermometer is irregular, it should be calibrated by the use of a 50-degree or 100-degree thread.

Ordinary high-temperature thermometers are tested most conveniently by comparison with a standard, or by taking readings at a series of known temperatures. High-temperature thermometers for a given limited range are kept of a reasonable length of stem and at the same time with an open scale by the insertion of intermediary bulbs which eliminate the undesired portions of the scale.*

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* Thermometric glasses and high-temperature thermometers are discussed in Hovestadt's "Jaener Glas" (in German and English), Mathias' "Les Modifications Permanentes du Verre," and in the publications of the Bureau of Standards. Guillaume's "Thermométrie de Précision" describes details of calibration and manipulation.

The glass of mercury thermometers has been successfully replaced by quartz, which is almost an ideal thermometric envelope, possessing an insignificant expansion and no appreciable zero lag, and capable of being used at very high temperatures. Such mercury-in-quartz thermometers are now constructed by Siebert and Kühn, and are graduated to about 700° C.

Dufour has tried to substitute tin for mercury-in-quartz thermometers, thereby attaining a temperature of over 1000° C. Such thermometers have not yet, however, come into use. It is a difficult matter, not yet satisfactorily solved, to find a substance suitable to use as thermometric fluid in quartz at high temperatures.

Fusing-point Pyrometry. — As long ago as 1827, Prinsep proposed to compare temperatures by means of the fusing points of certain metals and alloys. But the nonoxidizable metals are not numerous and all are relatively very costly: silver, gold, palladium, platinum. Use has, however, been made sometimes of these metals and their alloys, in admitting that the fusing point of a mixture of two substances is the arithmetical mean of the points of fusion of the components, which is not quite exact. The use of these alloys is entirely abandoned to-day, and with reason.

In a sense, this method of pyrometry may be said to be still in use, since the temperature scales of the several standardizing laboratories are practically defined by the freezing temperatures of pure metals.

By making use of *metallic salts*, among which a great number may be heated without alteration, one might construct a scale of fusing points whose use would be often very convenient; but this work is not yet done, at least not in a sufficiently precise manner. To the separate salts may be added their definite combinations and their eutectic mixtures which have perfectly definite fusing points. But any mixture whatever of two salts cannot be taken, because in general the solidification takes place throughout a large interval of temperature and in a progressive manner.

In some metallurgical operations, it is often necessary to be certain that objects are heated above some definite temperature. Salt baths of known freezing points, and of materials not attacking the metals used, serve excellently both for heating such objects and automatically giving the minimum temperature allowable.

We may cite in this connection the investigations of Brearley and Morewood and of Grenet on pure salts and eutectic and isomorphous mixtures suitable for this purpose. For the heat treatment of steels, Grenet recommends the following series of salts:

GRENET'S SERIES OF SALTS FOR HEAT TREATMENT OF STEELS.

	Melting point.		Melting point.
K_2SO_4	1070° C.	KCl	775° C.
$BaCl_2$	955	KBr	730
Na_2SO_4	865	KI	682
$5\,K_2SO_4+5\,Na_2SO_4$	850	$5.8\,KCl+4.2\,NaCl$	655
$3\,K_2SO_4+7\,Na_2SO_4$	830	$3\,NaCl+7\,KBr$	625
$2\,K_2SO_4+8\,Na_2SO_4$	825	$Ba(NO_3)_2$	600
Na_2CO_3	810	$Ca(NO_3)_2$	550
$NaCl$	800		

The uncertainty of our knowledge of the numerical values of the melting points of some of the salts is illustrated in the table on next page and in Chapter XI.

It would be worth while to carry out a careful series of determinations of the melting points of these and other salts, using the care and refinements of method that have been employed in recent work on metals, and employing large quantities of salt, 300 to 1000 grms.

"*Sentinel pyrometers*" and pastes, such as those of Brearley (The Amalgams Company, Sheffield), are also useful in certain operations. The former are cast in the form of small cylinders from molecular mixtures of salts. For temperatures below 500° C. they are inclosed in glass tubes and therefore last indefinitely, and for higher temperatures are placed in saucers (Fig. 129). Two such "sentinels" may be used, for example, to control a furnace within any given temperature range, the one being liquid and the other solid. The paste, made from salts mixed with

MELTING POINTS OF SALTS.

Date.	1896.	1894.	1903.	1905.
Authors.	Ramsay and Eumorfopoulos.	McCrae.	Ruff and Plato.	Hüttner and Tammann.
Method.	Meldometer.	Thermoelectric.	Thermoelectric.	Thermoelectric.
Calibration data.	$KNO_3=339$ $K_2SO_4=Au+7°$ $=1052$.	Diphenylamine $=304$ SBP$=445$ $Au=1072$.	Reichsanstalt scale.	$Sb=630.6$ $Au=1064$.
Quantity in grms.	0.001.	Small.	20.	25-40.
Na_2SO_4	884	883	880	897
Na_2CO_3	851	861	...	853
$NaCl$	792	813	820	810
$NaBr$	733	761	765	748
NaI	603	695	650	...
K_2SO_4	1052	1059	1050	1074
K_2CO_3	880	893	880	894
KCl	762	800	790	778
KBr	733	746	750	740
KI	614	723	705	680
Li_2SO_4	815	...	...	859
Li_2CO_3	618	...	...	734
$CaCl_2$	710	802	780	...
$SrCl_2$	796	854	...	...
$BaCl_2$	844	916	960	...

paraffin, is smeared onto the metal to be heated, and melting of the paste is readily recognized. The range covered by the sentinels and pastes is to 1070° C.

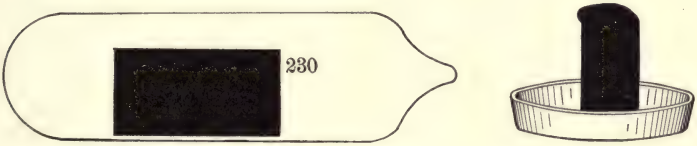


Fig. 129. Sentinel Pyrometers.

Any method based on the use of fusing points alone, whether metals, alloys, or salts, is evidently a discontinuous one, and has its main usefulness in processes where only a maximum or minimum temperature is required.

Fusible Cones. — Instead of utilizing the fusion of crystallized substances which pass abruptly from the solid to the liquid state, use may be made of the progressive softening of vitreous matters, that is to say, of mixtures containing an excess of one of the three acids, silicic, boric, or phosphoric. It is necessary in this case to have a definite process for defining a type degree of softening; a definite depression of a prism of given size is taken. These small prisms, formed of vitreous matters, are known under the name of *fusible cones*.

This method was first devised by Lauth and Vogt, who applied it in the manufactures at Sèvres before 1882. But they did not develop it as far as was possible; they were content to construct a small number of fusible cones corresponding to the various temperatures employed in the manufacture of the Sèvres porcelain.

Seger, director of a research laboratory at the royal pottery works of Berlin, published, in 1886, an important memoir on this question. He determined a whole series of fusible cones known as *Seger cones*, of intervals of about 25°, including the interval of temperature from 600° to 1800°. The substances which enter into the composition of these cones are essentially:

Pure quartz sand;
Norwegian feldspar;
Pure carbonate of lime;
Zettlitz kaolin.

The composition of this last is:

SiO_2	46.9
Al_2O_3	38.6
FeO_3	0.8
Alkalies	1.1
Water	12.7

In order to obtain very infusible cones, calcined alumina is added, and for very fusible cones oxide of iron, oxide of lead, carbonate of soda, and boric acid.

The shape of these cones (Fig. 130) is that of triangular pyramids of 15 mm. on a side and 50 mm. high. Under the action of heat, when softening begins, they at first contract without change of form, then they tip, bending over, letting their apex turn downwards, and finally flattening out completely. One says that the cone has fallen, or that it has melted, when it is bent halfway over, the point directed downwards.

The fusing points of these substances have been determined at the Berlin porcelain works by comparison with the Le Chatelier thermoelectric pyrometer, previously described.

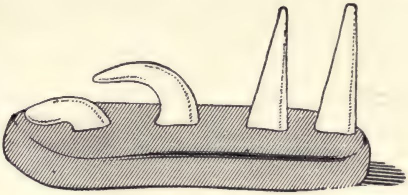


Fig. 130. Seger Cones.

The cones are numbered, for the less fusible, which were first adjusted, from 1 to 38; this last, the least fusible, corresponds to 1980°. The second series, more fusible, and established later, by Cramer and Hecht, is numbered from 01 to 022; this last cone, the most fusible, corresponds to 590°.

If, instead of using the cones of German make, one wishes to make them himself in employing the same formulæ, it is prudent to make a new calibration. The kaolins and feldspars from different sources never have exactly the same compositions, and very slight variations in their amounts of contained alkali may cause marked changes in the fusibility, at least for the less fusible cones. It is also well, on this account, to compare the behavior of new cones with old, even from the same maker.

It is to be noticed that in a great number of cones silica and alumina are found in the proportions $Al_2O_3 + 10\ SiO_2$. This is for the reason that this mixture is more fusible than can be had with silica and alumina alone. It is the starting point to obtain the other cones, the less fusible by the addition of alumina, and the more fusible by the addition of alkaline bases.

The table on pages 371 and 372 gives the list of cones of Seger's scale as they were originally issued.

These cones may be classed in a series of groups, in each of which the compositions of different cones are derived from that of one of them, generally the most fusible, by addition in varying proportions or sometimes by substitution of another substance.

The cones 28 to 38 are derived from the cone 27 by the addition of increasing quantities of Al_2O_3.

The cones 5 to 28 from the cone 5 by addition of increasing quantities of the mixture $Al_2O_3 + 10\ SiO_2$.

The cones 1 to 5 from the cone 1 by substitution of increasing quantities of alumina for the sesquioxide of iron.

The cones 010 to 1 from the cone 1 by the substitution of boric acid for silica.

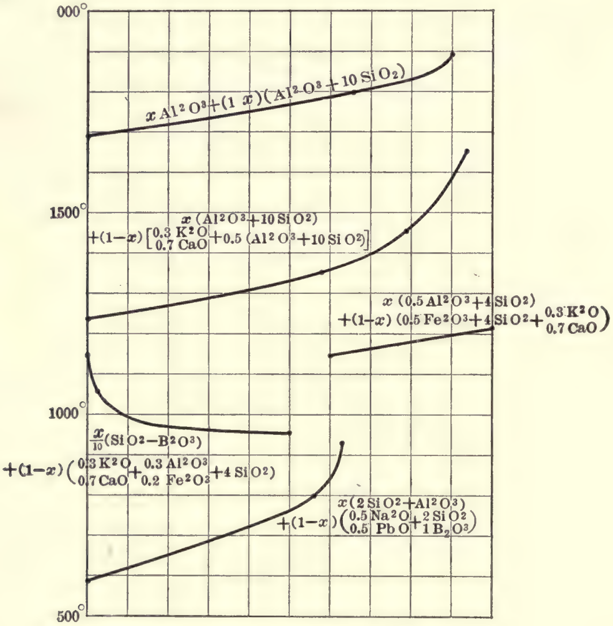


Fig. 131. Composition of Seger Cones.

The cones 022 to 011 from the cone 022 by the addition of increasing quantities of the mixture $Al_2O_3 + 2\ SiO_2$.

Fig. 131 gives the graphical representation of these data; the ordinates are temperatures, and the abscissæ are values of x from the table.

These fusible cones of Seger are pretty generally used in the ceramic industry; they are very convenient in all intermittent furnaces whose temperature has to increase constantly up to a certain maximum, at which point the cooling off is allowed to commence. It is sufficient, before firing up, to place a certain number of fusible cones opposite a draft hole closed by a glass, through which they may be watched. In seeing them fall successively, one knows at what moments the furnace takes on a series of definite temperatures.

In continuous furnaces, the cones may be put into the furnace during the process, but that is more delicate. It is necessary to place them on little earthenware supports that are moved into the desired part of the furnace by an iron rod. When, on the contrary, they are put in place at the start in the cold furnace, they are held in place by a small lump of clay.

THE ORIGINAL SEGER CONE SCALE.

Nos.	Deg. C.	Composition.	X	Formulæ.
38	1890	1 $Al_2O_2+1\ SiO_2$	9	$XAl_2O_3 + (1-X)(Al_2O_3 + 10\ SiO_2)$
36	1850	1 " $+1.5$ "	8	
35	1830	1 " $+2$ "		
34	1810	1 " $+2.5$ "		
33	1790	1 " $+3$ "		
32	1770	1 " $+4$ "		
31	1750	1 " $+5$ "		
30	1730	1 " $+6$ "		
29	1710	1 " $+8$ "		
28	1690	1 " $+10$ "		
27	1670	1 $\left\{\begin{matrix}0.3\ K_2O\\ 0.7\ CaO\end{matrix}\right\}+20(Al_2O_3+10\ SiO_2)$	0	$X(Al_2O_3+10\ SiO_2) + (1-X)\left(\left\{\begin{matrix}0.3\ K_2O\\ 0.7\ CaO\end{matrix}\right\} + 0.5(Al_2O_3+10\ SiO_2)\right)$
26	1650	1 " $+7.2$ "	93	
25	1630	1 " $+6.6$ "		
24	1610	1 " $+6$ "		
23	1590	1 " $+5.4$ "		
22	1570	1 " $+4.9$ "		
21	1550	1 " $+4.4$ "		
20	1530	1 " $+3.9$ "		
19	1510	1 " $+3.5$ "		
18	1490	1 " $+3.1$ "		
17	1470	1 " $+2.7$ "		
16	1450	1 " $+2.4$ "	79	
15	1430	1 " $+2.1$ "		
14	1410	1 " $+1.8$ "		
13	1390	1 " $+1.6$ "		
12	1370	1 " $+1.4$ "		
11	1350	1 " $+1.2$ "	58	
10	1330	1 " $+1$ "		
9	1310	1 " $+0.9$ "		
8	1290	1 " $+0.8$ "		
7	1270	1 " $+0.7$ "		
6	1250	1 " $+0.6$ "		
5	1230	1 " $+0.5$ "	0	
4	1210	1 " $+0.5\ Al_2O_3+4\ SiO_2$	1	$X\ (0.5\ Al_2O_3+4\ SiO_2) + (1-X)\ .\ (0.5\ Fe_2O + 4\ SiO_2+0.7\ CaO)$
3	1190	1 " $+\left\{\begin{matrix}0.45\ Al_2O_3\\ 0.05\ Fe_2O_3\end{matrix}\right\}+4\ SiO_2$		
2	1170	1 " $+\left\{\begin{matrix}0.4\ Al_2O_3\\ 0.1\ Fe_2O_3\end{matrix}\right\}+4\ SiO_2$		
1	1150	1 " $+\left\{\begin{matrix}0.3\ Al_2O_3\\ 0.2\ Fe_2O_3\end{matrix}\right\}+4\ SiO_2$		

THE ORIGINAL SEGER CONE SCALE (*Continued*).

Nos.	Deg. C.	Composition.	X	Formulæ.
01	1130	$1\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}+\left\{\begin{matrix}0.3\ Al_2O_3\\0.2\ Fe_2O_3\end{matrix}\right\}+\left\{\begin{matrix}3.95\ SiO_2\\0.05\ B_2O_3\end{matrix}\right\}$	1.05	$\frac{X}{10}(SiO_2-B_2O_3)+(1-X)\left(\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}+\left\{\begin{matrix}0.3\ Al_2O_3\\0.2\ Fe_2O_3\end{matrix}\right\}+4\ SiO_2\Big)$
02	1110	1 " + " $+\left\{\begin{matrix}3.90\ SiO_2\\0.10\ B_2O_3\end{matrix}\right.$		
03	1090	1 " + " $+\left\{\begin{matrix}3.85\ SiO_2\\0.15\ B_2O_3\end{matrix}\right.$		
04	1070	1 " + " $+\left\{\begin{matrix}3.80\ SiO_2\\0.20\ B_2O_3\end{matrix}\right.$		
05	1050	1 " +1 " $+\left\{\begin{matrix}3.75\ SiO_2\\0.25\ B_2O_3\end{matrix}\right.$	1.25	
06	1030	1 " +1 " $+\left\{\begin{matrix}3.70\ SiO_2\\0.30\ B_2O_3\end{matrix}\right.$		
07	1010	1 " +1 " $+\left\{\begin{matrix}3.65\ SiO_2\\0.35\ B_2O_3\end{matrix}\right.$		
08	990	1 " +1 " $+\left\{\begin{matrix}3.60\ SiO_2\\0.40\ B_2O_3\end{matrix}\right.$		
09	970	1 " +1 " $+\left\{\begin{matrix}3.55\ SiO_2\\0.45\ B_2O_3\end{matrix}\right.$		
010	950	1 " +1 " $+\left\{\begin{matrix}3.5\ SiO_2\\0.5\ B_2O_3\end{matrix}\right.$	5	
011	920	$1\left\{\begin{matrix}0.5\ Na_2O\\0.5\ PbO\end{matrix}\right\}+0.8\ Al_2O_3+\left\{\begin{matrix}3.6\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$	0.62	$X(2\ SiO_2+Al_2O_3)+(1-X)\left(\begin{matrix}0.5\ Na_2O\\0.5\ PbO_3\end{matrix}\right\}+\left\{\begin{matrix}2\ SiO_2\\1\ B_2O_3\end{matrix}\right\}\Big)$
012	890	1 " +0.75 " $+\left\{\begin{matrix}3.5\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$		
013	860	1 " +0.70 " $+\left\{\begin{matrix}3.4\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$		
014	830	1 " +0.65 " $+\left\{\begin{matrix}3.3\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$		
015	800	1 " +0.60 " $+\left\{\begin{matrix}3.2\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$	0.57	
016	770	1 " +0.55 " $+\left\{\begin{matrix}3.1\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$		
017	740	1 " +0.50 " $+\left\{\begin{matrix}3.0\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$		
018	710	1 " +0.40 " $+\left\{\begin{matrix}2.8\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$		
019	680	1 " +0.30 " $+\left\{\begin{matrix}2.6\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$		
020	650	1 " +0.20 " $+\left\{\begin{matrix}2.4\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$		
021	620	1 " +0.10 " $+\left\{\begin{matrix}2.2\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$		
022	590	1 " $+\left\{\begin{matrix}2.0\ SiO_2\\1.0\ B_2O_3\end{matrix}\right.$	0	

Recent investigations on Seger cones, in view of their improvement, have been carried out mainly by the staff of the Laboratorium für Tonindustrie, and at the Reichsanstalt, and consequently there have been changes in their composition, melting point, and numbering. The improvements have been mainly in increasing the sharpness of melting points, elimination in so far as possible of the lag due to rate of heating, and finding components that are uninfluenced by the usual ceramic furnace atmosphere. This has resulted in the elimination of lead and iron compounds. Cones Nos. 21 to 25 have been dropped, as their melting points were too close together; and four new cones, Nos. 39 to 42, the most refractory of all, have been added.

In the following table are given the melting points of the cones according to the Tonindustrie Zeitung circulars for 1910, together with their compositions when the latter differ from the original series.

1910 SCALE OF SEGER CONES.

No.	Deg. C.	Composition.
42	2000	Al_2O_3
41	1960	Al_2O_3 0.13 SiO_2
40	1920	Al_2O_3 0.33 SiO_2
39	1880	Al_2O_3 0.66 SiO_2
38	1850	
37	1825	
36	1790	
35	1770	
34	1750	
33	1730	
32	1710	
31	1690	
30	1670	
29	1650	

No.	Deg. C.	No.	Deg. C.
28	1630	14	1410
27	1610	13	1380
26	1580	12	1350
20	1530	11	1320
19	1520	10	1300
18	1500	9	1280
17	1480	8	1250
16	1460	7	1230
15	1435		

No.	Deg. C.	Composition.		
6a	1200	0.013 Na_2O 0.288 K_2O 0.685 CaO 0.014 MgO	0.693 Al_2O_3	6.801 SiO_2 0.026 B_2O_3
5a	1180	0.028 Na_2O 0.274 K_2O 0.666 CaO 0.032 MgO	0.684 Al_2O_3	6.565 SiO_2 0.056 B_2O_3
4a	1160	0.043 Na_2O 0.260 K_2O 0.649 CaO 0.048 MgO	0.676 Al_2O_3	6.339 SiO_2 0.086 B_2O_3
3a	1140	0.059 Na_2O 0.244 K_2O 0.630 CaO 0.067 MgO	0.667 Al_2O_3	6.083 SiO_2 0.119 B_2O_3
2a	1120	0.085 Na_2O 0.220 K_2O 0.599 CaO 0.096 MgO	0.652 Al_2O_3	5.687 SiO_2 0.170 B_2O_3
1a	1100	0.109 Na_2O 0.198 K_2O 0.571 CaO 0.122 MgO	0.639 Al_2O_3	5.320 SiO_2 0.217 B_2O_3

1910 SCALE OF SEGER CONES (*Continued*).

No.	Deg. C.	Composition.		
01a	1080	0.134 Na_2O 0.174 K_2O 0.541 CaO 0.151 MgO	0.625 Al_2O_3	4.931 SiO_2 0.268 B_2O_3
02a	1060	0.157 Na_2O 0.153 K_2O 0.513 CaO 0.177 MgO	0.611 Al_2O_3	4.572 SiO_2 0.314 B_2O_3
03a	1040	0.182 Na_2O 0.130 K_2O 0.484 CaO 0.204 MgO	0.598 Al_2O_3	4.199 SiO_2 0.363 B_2O_3
04a	1020	0.204 Na_2O 0.109 K_2O 0.458 CaO 0.229 MgO	0.586 Al_2O_3	3.860 SiO_2 0.407 B_2O_3
05a	1000	0.229 Na_2O 0.086 K_2O 0.428 CaO 0.257 MgO	0.571 Al_2O_3	3.467 SiO_2 0.457 B_2O_3
06a	980	0.247 Na_2O 0.069 K_2O 0.407 CaO 0.277 MgO	0.561 Al_2O_3	3.197 SiO_2 0.493 B_2O_3
07a	960	0.261 Na_2O 0.055 K_2O 0.391 CaO 0.293 MgO	0.554 Al_2O_3	2.984 SiO_2 0.521 B_2O_3
08a	940	0.279 Na_2O 0.038 K_2O 0.369 CaO 0.314 MgO	0.543 Al_2O_3	2.691 SiO_2 0.559 B_2O_3
09a	920	0.336 Na_2O 0.018 K_2O 0.335 CaO 0.311 MgO	0.468 Al_2O_3	3.087 SiO_2 0.671 B_2O_3
010a	900	0.338 Na_2O 0.011 K_2O 0.338 CaO 0.313 MgO	0.423 Al_2O_3	2.626 SiO_2 0.675 B_2O_3
011a	880	0.349 Na_2O 0.340 CaO 0.311 MgO	0.4 Al_2O_3	2.38 SiO_2 0.68 B_2O_3
012a	855	0.345 Na_2O 0.341 CaO 0.314 MgO	0.365 Al_2O_3	2.04 SiO_2 0.68 B_2O_3

1910 SCALE OF SEGER CONES (*Continued*).

No.	Deg. C.	Composition.		
013a	835	0.343 Na_2O 0.343 CaO 0.314 MgO	0.34 Al_2O_3	1.78 SiO_2 0.69 B_2O_3
014a	815	0.385 Na_2O 0.385 CaO 0.230 MgO	0.34 Al_2O_3	1.92 SiO_2 0.77 B_2O_3
015a	790	0.432 Na_2O 0.432 CaO 0.136 MgO	0.34 Al_2O_3	2.06 SiO_2 0.86 B_2O_3
016	750	Bf.*	0.31 Al_2O_3	1.61 SiO_2 1 B_2O_3
017	730	Bf.	0.2 Al_2O_3	1.4 SiO_2 1 B_2O_3
018	710	Bf.	0.13 Al_2O_3	1.26 SiO_2 1 B_2O_3
019	690	Bf.	0.08 Al_2O_3	1.16 SiO_2 1 B_2O_3
020	670	Bf.	0.04 Al_2O_3	1.08 SiO_2 1 B_2O_3
021	650	Bf.	0.02 Al_2O_3	1.04 SiO_2 1 B_2O_3
022	600			

$$* \mathrm{Bf} = \left\{ \begin{array}{l} 0.50\ Na_2O \\ 0.25\ CaO \\ 0.25\ MgO \end{array} \right.$$

It would seem to be well to replace, in so far as possible, these cones by pure compounds and eutectics having definite melting points, as the softening temperatures of the former are influenced considerably, in some cases 100° C. or more, by the rate of heating, as has been remarked by several investigators. Dr. Kanolt of the Bureau of Standards has carried out a series of measurements on some of the "Standard Pyrometric Cones" of Professor Orton of the Ohio State University, corresponding to Nos. 25 to 36 of the Seger series, as well as on this Seger series. His work shows that heating the cones as rapidly as 5° C. per minute, when near their softening temperatures, will give too high values for these temperatures. The rate of heating in the experimental or calibrating furnace must be reduced to more nearly that which obtains in kiln practice, in order to get a fair calibration of the cones for use in the ceramic industries.

The Seger and Orton cones were found to agree very closely in their behavior. With slow heating, the cones of the series 25–36 were found to soften at temperatures lower by 40° to 70° C. than indicated in the table of 1910, page 373, agreeing closely in this with the results found by Heræus. Melting in air or in vacuo gave the same results. Kanolt's measurements were made with an optical pyrometer whose scale is represented by Au = 1064°, Pd = 1550°, Pt = 1755° C.

At the Reichsanstalt, Hoffmann and Meissner find (1911) similar differences between softening temperatures in ceramic kilns for a time of heating of about sixty hours and in the electric furnace.

SOFTENING TEMPERATURES OF SEGER CONES.

Cone number.	In electric furnace.	In ceramic kiln.	Difference.
4	1225	1160	65
6	1260	1200	>60
7	1285	1180	105
8	1305	<1200	105
9	1335	1225	110
10	1345	1235	110
13	1395	1315	80
14	1415	1375	40
16	1460	1405	55
17	1480	1410	70

On the whole, it may be said that the Seger cone series give reliable relative temperatures to about 25° C. at the higher temperatures for any given method of procedure, but too much reliance should not be placed on the numerical values of the temperatures apparently measured.

Wiborgh's Thermophones. — Another cheap, discontinuous pyroscope has been put on the market by Wiborgh. His thermophones are refractory earth cylinders 2.5 cm. long and 2 cm. in diameter, containing an explosive. A thermophone is quickly deposited in the region whose temperature is sought, and the time noted to the fifth of a second until the cylinder bursts. A table then gives the temperature. Very concordant results are obtained if the thermophones are kept dry, different cylinders of the same set agreeing to one-fifth second, or 20° C. at 1000° C.

Dilution Pyrometers. — If a current of liquid or gas is kept flowing through a heated space, it is evidently possible to estimate the temperature of the latter by observing the inlet and outlet temperatures of the fluid. Carnelly and Burton constructed such a pyrometer, using water flowing at constant head from a tank kept at constant temperature. The graduation of such a pyrometer is purely empirical, and may be effected, for a given heat and temperature of supply, by taking the inlet and outlet temperatures for three or more known temperatures of the furnace. For every different head and temperature of source the graduation will be different. Such a pyrometer evidently requires a somewhat cumbersome, permanent installation, and has the further disadvantages of not being direct-reading and having its indications change with difficultly controllable factors.

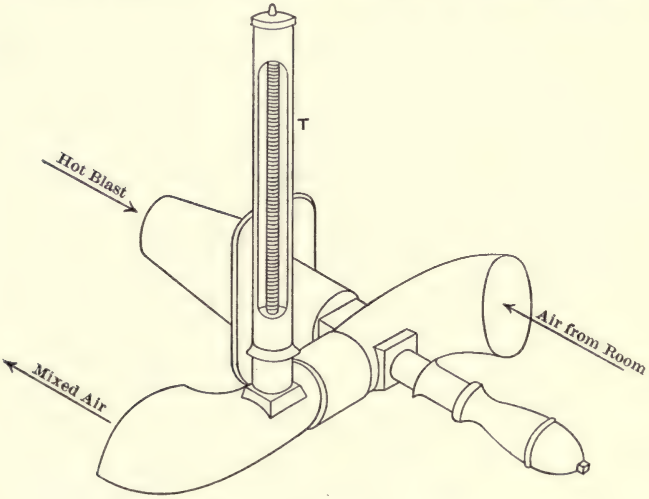


Fig. 132. Hot-blast Pyrometer.

For determining hot-blast temperatures air-dilution pyrometers have been used, air from the outside entering the blast, mixing with it, and the temperature of the outcoming mixture being taken with a mercury thermometer, and then the temperature of the blast computed from an empirical calibration. But very uncertain results can be obtained in this way, as they will depend on the speed of the blast, the size of openings, and the temperature of the diluting air. Such a pyrometer is illustrated in Fig. 132.

Pyrometers, such as Carnelly's, have also been based on the circulation of a water stream whose inlet and outlet temperatures could be taken.

Transpiration Pyrometers. — Various attempts have been made to construct pyrometers based on the variation of the viscosity of gases with temperature, and this subject has been thoroughly studied by Holman, Barus, and Callendar; but, owing to the complexity of the viscosity temperature relation for small tubes, no simple pyrometer based on this relation alone, not requiring an arbitrary calibration, has been devised. This method may perhaps serve, as first suggested by Barus, as an independent one for extending the temperature scale beyond the region reached by other forms of gas thermometer.

Job has shown that if a short piece of platinum wire be inserted in the end of a porcelain tube of less than 1 mm. diameter and a *constant* current of gas, as from an electrolytic cell or blower, be passed through this capillary, the back pressure developed will be proportional to the temperature, or $T = k(H - h_0)$, where H is given by a manometer inserted between the cell or blower and the porcelain capillary, and h_0 is the initial pressure. This simple relation holds very exactly up to temperatures as high as 1500° C., and the method may be made very sensitive by a proper choice of manometer liquid and initial pressure h_0. The indications, however, vary with the depth of immersion of the capillary, and they depend not alone upon the viscosity of the gas, but also upon the relative expansion of platinum and porcelain.

A pyrometer depending upon the change in pressure produced in a current of gas or vapor passing through a small orifice A (Fig. 133), at high temperature has been developed by Uhling and

Steinbart, using a steam-jacket aspirator *D* to produce a steady flow. It is essential that the air pass through the apertures *B* and *A* at a constant pressure, as measured by *Q*, that all the air become heated to a uniform temperature at *A*, that the apertures, which are but pinholes, remain perfectly clear, that the temperature of the colder aperture *B* remain constant, and that there are no leaks. The hot end *CA* is inclosed within a tube of platinum or nickel and the air is filtered before passing into *A*.

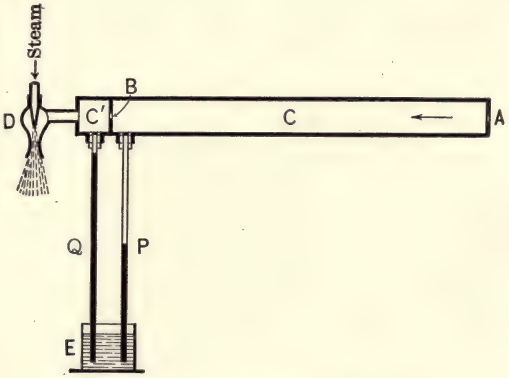


Fig. 133. Uhling-Steinbart Pyrometer.

Although simple in principle, the apparatus as constructed is very complicated and costly. It is made direct-reading and also recording. The calibration is empirical and the apparatus is so constructed that temperatures are read off the water-manometer column, *P*. The elaborateness of construction of such a pressure apparatus renders it liable to deteriorate with time and use, and it requires a source of steam for its operation.

In Threw's pyrometer, air under constant pressure is forced through a coiled tube in the heated region, and the back pressure developed between a hot and cold orifice is measured on a water column in much the same way as in Uhling's apparatus. Both these instruments have been used considerably in blast-furnace practice.

Vapor-pressure Pyrometers. — Use is made of the fact that the pressure of a saturated vapor, or one in the presence of its liquid, depends only on the temperature of the vapor, and is independent of its volume. Readings of such a pyrometer may reduce to those of a pressure gauge. There is an apparent advantage over the gas thermometer, in that the volume of the containing vessel plays no part. This vessel must be gas-tight, however, in both types. For relatively low temperatures, where ether or water may be used, to 350° C. for water, several industrial forms using this principle have been developed, that have given satisfaction in special installations, notably the thalpotassimeter of Schaffer and Budenberg and the instruments of Fournier.

The difficulty of rendering them gas-tight and permanent when mercury or other substance suitable for higher temperatures is used appears to be a serious obstacle to the general introduction of this type of instrument as a pyrometer.

Other Pyrometric Methods. — We have by no means exhausted the list of methods for measuring high temperatures that have been suggested or tried. Without dwelling on any of them, we may mention a few that may possibly be of service in particular cases. The variation of boiling point with pressure of such substances as naphthaline, benzophenone, and sulphur, first studied in detail by Crafts, in 1882, will give a continuous temperature scale of very great range, although a relatively complicated pressure apparatus is necessary. Again, the velocity of sound in any medium is a function of its temperature; and, as early as 1837, a method of temperature measurement using this principle was devised by Cagniard-Latour with dry air as the medium. Other phenomena of less promise which have been made use of or suggested, are: heat conduction, rotary polarization, magnetic moment, dissociation, conductivity of gases and vapors, the corpuscular emission in vacuo from current-bearing metals, and an application of Clapeyron's Equation.

CHAPTER X.

RECORDING PYROMETERS.

Among the different methods for the measurement of high temperatures, some of them may be made continuously recording. This is as useful for industrial applications as for scientific investigations. In research laboratories one endeavors as much as possible to take observations automatically, escaping the influence either of preconceived ideas or of carelessness of the observer; in industrial works the use of such processes gives continuous control over the work of the artisans, such as the presence of no foreman can replace.

In recent years, one of the most important practical advances that have been made in pyrometry is the development of several types of simple, convenient, and reliable instruments for the registration of temperatures in industrial operations. It will be impossible to describe them all here, but we shall pass in review several, as well as calling attention to the historical development of the subject. Forms of temperature-recording apparatus, suitable for laboratory investigations of problems involving temperature changes, but too complicated for any but the most elaborate technical installations, have been in existence for a good many years, and the recent introduction of more simple apparatus has greatly stimulated technical research as well as afforded means for the exact control of a great many industrial operations that were heretofore left to chance.

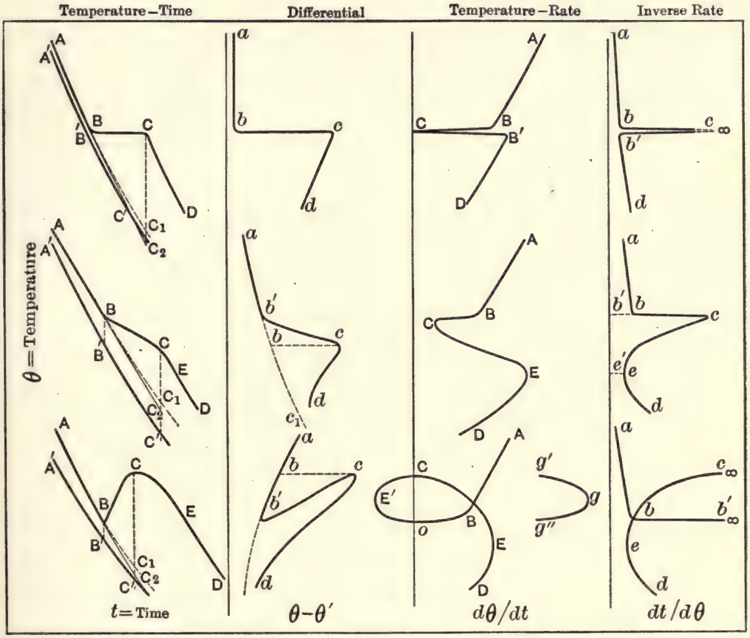
Forms of Temperature Records. — There are several ways in which the change of temperature with time may be recorded, and the method adopted will depend upon the problem in hand. The simplest and the one of most universal application and general utility both in the works and laboratory is the *time-temperature* curve; that is, the time appears as one coördinate, and the temperature, or some quantity proportional to it, as the other on the record sheet. Most temperature recorders are constructed on this basis. For a given temperature interval, there is evidently a limiting sensibility beyond which any such recorder cannot go without unduly increasing the size of the record sheet unless it is operated in steps, when of course the apparatus becomes only semi-recording and requires the occasional intervention of the operator.

In certain investigations in the laboratory it is of interest to have the rate of change of temperature in terms of the temperature, or the *temperature-rate* curve. Thus, in the study of definite phenomena, such as fusion and allotropic transformations, and in order to recognize their occurrence, use is ordinarily made of the accompanying absorption or liberation of heat, which is manifested by a variation in the rate of heating or cooling. Methods of recording the temperature-rate curve have been devised by Le Chatelier and by Dejean.

In the two preceding methods, any accidental variation in the temperature of the furnace, due to drafts or other outside causes, or to change in rate of heating or cooling, will be recorded. This is most desirable in those cases in which the changes in temperature of the furnace or its contents are wanted. But in those cases in which the transformations going on within the substance itself within the furnace are wanted, as, for example, when taking the cooling curve of a sample of steel, the accidental fluctuations in the heat content not inherent to the sample must be eliminated in exact work. This may be done, as shown by the late Sir Roberts-Austen, by taking the *differential-temperature* curve, or recording the temperature of the sample in terms of the successive differences in temperature between the sample under observation and another body, called the neutral, possessing no transformation points, and placed within the furnace close to the sample.

Although there are other methods of reading and interpreting temperature curves, the above are the only ones that have heretofore been made self-recording. We shall describe types of apparatus using all three methods.

Types of Cooling Curves. — It is of interest to be able to recognize the appearance of a transformation region as defined, for example, on cooling by the various methods above mentioned. In Fig. 134 are illustrated these various forms of temperature curves, in which θ = temperature and t = time for the three following cases: in the first line, the heat evolution balances the radiation and other losses during the transformation or the temperature remains constant, as in freezing of a pure substance well inclosed; in the second line, the most common, the transformation takes place over a definite temperature interval or there is imperfect heat insulation; and in the third, there is recalescence, or the reaction or transformation evolves heat so rapidly as to cause a rise in temperature. The nomenclature is the same for all the curves, and they may be compared by noting the corresponding letters.



TYPES OF COOLING CURVES

Fig. 134. Types of Cooling Curves.

We have included also the *inverse-rate* curve of Osmond, obtained by noting the time intervals necessary to cool equal decrements of temperature plotted in terms of temperature. Although this curve cannot be recorded automatically without elaborate apparatus, the inverse-rate method is one in very common use in metallographic practice. Rosenhain uses still another form of curve, the *derived-differential*, or the temperature difference between sample and neutral for equal temperature decrements plotted in terms of temperature. The observations are taken as if for the differential curve.

On the whole, the most complete, satisfactory, conveniently recorded, and readily interpreted results are obtained over long temperature intervals by the simultaneous recording or observing of the time-temperature and differential curves; or, as we shall see, it is possible to combine these two into a single curve giving differences between sample and neutral in terms of temperature. The time may also be indicated if desired in this latter case by a suitable interrupter.

The inverse-rate curve may be taken with great precision on a chronograph in connection with a potentiometer, the observer pressing a key at equal steps on the dials, and this method may be made as accurate as desired if automatic control of the furnace is provided. The form of the curve obtained is exactly the same as that with the derived differential method. These two methods may be applied simultaneously to advantage on the same sample, as is the practise at the Bureau of Standards.

Methods of Recording. — The recording may be effected either photographically, or by some electrical or mechanical means for which we may use the term "autographic". The latter possesses the advantage that the experimenter may watch any part of the record, and can therefore control the operation and at any moment vary the conditions affecting the experiment or process; whereas, with the photographic apparatus, it is usually necessary to wait until the plate is developed to see what has happened. The manipulation by the photographic method is usually also more delicate and time-consuming and the adjustment less sure, and the record often requires further graphical interpretation, for all of which reasons the photographic method is not adapted for most industrial needs. The autographic method is in general not adapted for interpreting phenomena taking place within an interval of a few seconds, so that for very rapid temperature changes it is usually necessary to employ the photographic method. An autographic recorder is usually the less readily adjusted for very variable rates, and most types of such apparatus are limited to one or two speeds. This is not a serious inconvenience, however, except in case of the use of the same instrument for very diverse purposes.

The following pyrometers have been made recording:

The constant-volume gas thermometer;
The thermoelectric pyrometer;
The electrical resistance pyrometer;
The total-radiation pyrometer;
The transpiration pyrometer.

The optical pyrometer of the Morse type could be made semi-recording, but the other optical and discontinuous types of pyrometer could be made recording only with very great difficulty.

Recording Gas Pyrometer. — The transformation of the gas pyrometer into a recording instrument is extremely simple and has been long since effected. It suffices to join permanently the tube from the porcelain bulb to a registering manometer to realize a recording pyrometer theoretically perfect. But practically these instruments possess many disadvantages that have prevented their introduction generally, and they have been replaced for the most part by other types more suitable both for laboratory and technical plants.

Above 1000° the permeability of the porcelain for water vapor is sufficient to soon render them useless. Investigations made by the Paris Gas Company have shown that in furnaces heated to 1100° the penetration of water vapor is sufficiently rapid so that in a few days liquid water collects in the cold parts of the apparatus.

Absolute impermeability of the apparatus, which is quite indispensable, since its operation supposes the invariability of the gaseous mass, is very difficult to obtain. Frequently the glazing of the porcelain has holes in it. The numerous joints entering into the registering apparatus, and above all the metallic parts of the apparatus, may be the seats of very small leakages difficult to locate.

The connection of the metallic parts with the porcelain tube is generally made with wax, always with substances of organic origin, which, in the vicinity of industrial apparatus, generally bulky and thick-walled, cannot be protected against radiation save by a water jacket. This is a serious inconvenience.

In laboratory apparatus of small size the protection of the joint is easier, but then the large dimensions of the bulb, as has been indicated, are a serious disadvantage. One cannot, in a small furnace, find a large volume whose temperature is uniform.

Another most serious disadvantage of the recording gas pyrometer is the difficulty of its calibration. Already with the mercury manometer the dead space is a source of complications. However, this may be measured and allowed for. With the registering manometer the dead space is much greater, and besides variable with the deformation of the elastic tube. Thus the calibration can be made only empirically, employing baths of fixed fusing or boiling points, an operation almost always impossible of realization with an apparatus of very fragile porcelain, or by using a large tube furnace whose temperatures are given by another type of pyrometer calibrated at the requisite fixed points. The recording gas thermometer is therefore of little practical interest.

Electrical Resistance Recording Pyrometer. — There have been several satisfactory solutions of the problem of rendering the resistance pyrometer self-registering.

Callendar's Slidewire Recorder. — In order to render his pyrometer recording (Figs. 135 and 137), Callendar employs the following very simple device: Two of the branches of a Wheatstone bridge used to measure the resistance of the heated coil are made of a single wire, on which slides a rider to which is brought one of the galvanometer leads. To each position of the rider, when the galvanometer is at zero, corresponds a resistance, and consequently a definite temperature of the coil. The position of the rider may be easily registered by attaching to it a pen writing on a sheet of paper which moves perpendicularly to the length of the wire. In order to have the curve thus obtained correspond to that of temperatures, it suffices that the position of the rider be at each instant adjusted so as to keep the galvanometer at zero.

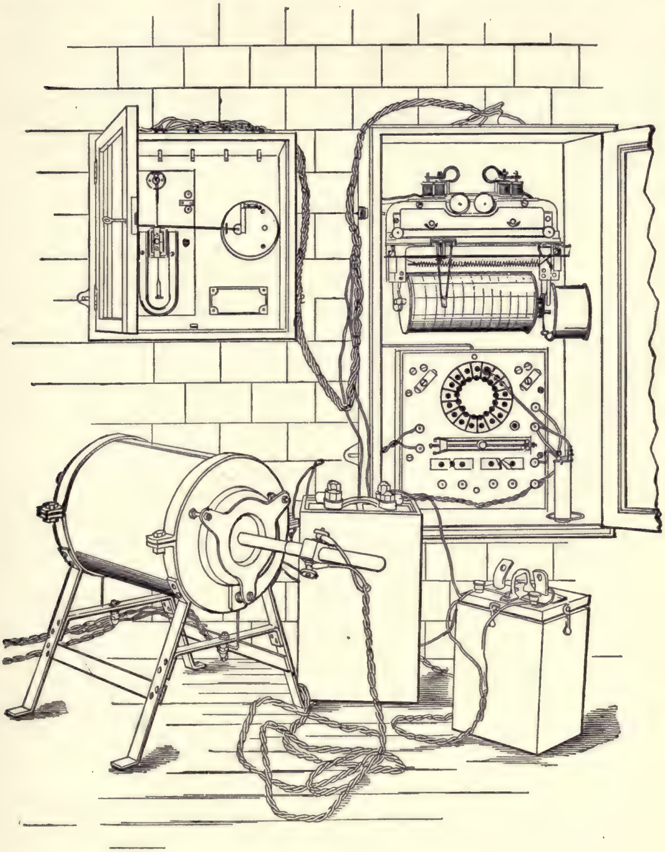


Fig. 135. Callendar's Recorder.

This result is obtained by means of a clock movement controlled by a relay that the galvanometer works in one direction or the other, according to the direction of the deflection that it tends to take on from the zero point. It is a movable-coil galvanometer whose needle carries an arm which, making contact, causes a current to pass. The curve traced by this instrument is in rectangular coördinates, which is of practical convenience in reading off temperatures.

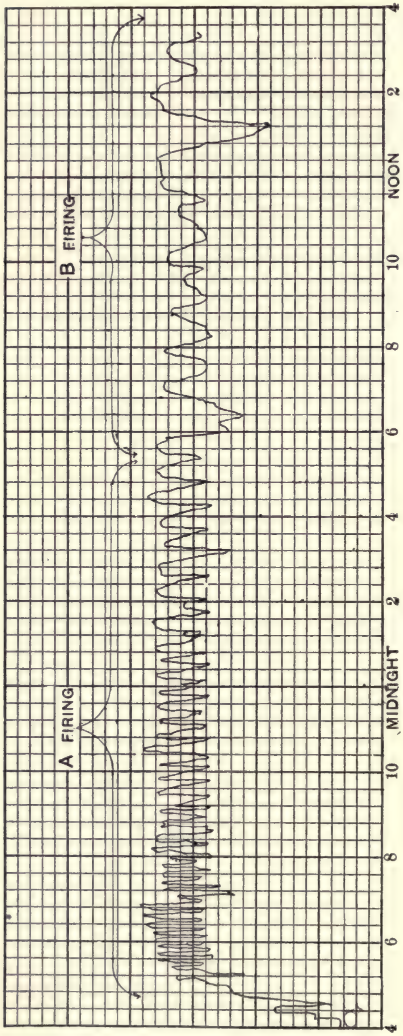


Fig. 136. Record with Callendar Recorder.

Fig. 136 gives an example of a curve recorded by this apparatus, showing the effect on the temperature of an annealing oven by firing by an old hand and by a new one. It will be noted that a continuous pen record is obtained.

This recorder possesses an interesting detail which assures good working and which could well be adopted in other similar cases. The pointer of the galvanometer needle does not hit against a fixed conductor, to which it would stick on account of heating by the passage of the current and especially the extra current at break. This conductor consists of the metallic circumference of a wheel which is given a slow, constant rotary motion, rendering all adherence impossible. This artifice renders possible working the relays by means of a sensitive galvanometer, which would not otherwise be realizable.

This registering apparatus is necessarily very costly, but until recently was the only sensitive one generally available with which a record of high temperatures could be obtained by purely mechanical means without the intervention of photography. This apparatus labors further under the disadvantages inherent to a somewhat complicated mechanism, requiring the intervention of skilled labor to adjust it; nevertheless, it has proved of extreme usefulness in many technical operations requiring exact temperature control, especially in large works.

For use in the laboratory, it is to be noted that some of the extreme sensitiveness of the resistance method of measuring temperatures is necessarily lost by rendering it recording; but such loss is not serious enough to prevent this, the most sensitive method of recording, to be of great use in many laboratory investigations. A sensibility of 1 in 5000 may easily be maintained, and with care considerably higher sensibility. The relatively large volume of the bulb, or thermometric coil, is sometimes a disadvantage, as in taking cooling curves of steel specimens. Callendar calls attention also to the following points: The scale of the instrument is uniform and independent of the E.M.F. of the battery, being determined by the resistance of the bridge wire in relation to that of the thermometer, and these may be constructed to give any desired temperature range. It is a great advantage in practice that the scale never requires adjustment, but is always correct to about 1 in 1000, provided the bridge wire is correct and uniform.

For ordinary work, thermometers are generally provided with an "ice bobbin" or balancing coil, for adjusting the resistance of the thermometer at 0° C. The ice bobbin for each thermometer is connected to its appropriate terminals when the thermometer to which it belongs is in use. If the thermometer is required to cover an extensive range of temperature, and it is desired to keep the sensitiveness very great, a series of auxiliary resistances or "zero coils," generally ranging from 0 to 20 ohms, may be provided, which enables the range to be extended to twenty times that of the 1-ohm bridge wire. With a 26-ohm thermometer the range thus obtained would be 200° C., or 2000° C. with a 2.6-ohm pyrometer.

The most important points to test in a slide-wire recorder are the adjustment of the zero of the galvanometer and the zero of the slide wire. The former is effected by turning the torsion lead of the suspension until the galvanometer boom swings clear of the contact wheel; and for the latter, the slide wire itself may be shifted with respect to the record paper, the pyrometer and compensation terminals being short-circuited and the battery switched on.

This recorder, as well as the others we shall mention, may be arranged to register any of the component factors in electric power, and may therefore serve also as a thermoelectric recorder.

When so used for the measurement of temperatures by means of thermoelectric couples by the method of opposition, the strength of the currents available to work the relays is much more feeble than in the preceding applications, so that a great sensibility cannot be obtained. Fig. 136 shows a Callendar recorder as made by the Cambridge Instrument Company, arranged for the thermoelectric measurement of temperatures in connection with an electric resistance furnace. In Fig. 137 is shown the wiring diagram for a Callendar recorder arranged for commercial work.

Deflectional Recorders. — The thread recorder, shown in Fig. 152, or other type of recording millivoltmeter designed primarily for use with thermocouples, may also be used to register relatively small intervals of temperature when used as the deflecting galvanometer of a Wheatstone bridge for a resistance thermometer, provided the sensitiveness of the recording instrument is sufficient. This is readily accomplished, since a high-resistance galvanometer is not required nor desired. In Fig. 138 is shown such an arrangement as used by Callendar. The

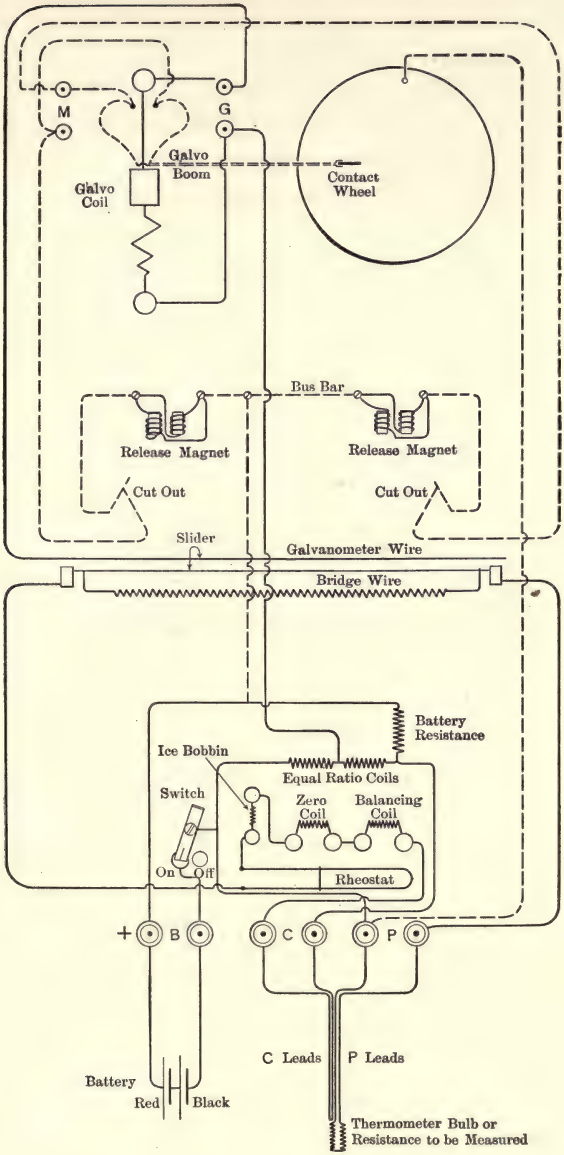


Fig. 137. Wiring Diagram, Callendar Recorder.

Siemens and Halske recorder (Fig. 149) may also be had with a very sensitive scale, i.e., 1.5 millivolt, for example, for a galvanometer resistance of 10.5 ohms.

Some form of platinum-thermometer bridge with a slide wire is required, and a rheostat capable of fine adjustment. This rheostat is connected in series with a storage cell and serves to adjust the scale of the record. One terminal of the recorder is connected at G between the ratio arms of the bridge B_1G and B_2G, and the other to the sliding contact on the bridge wire.

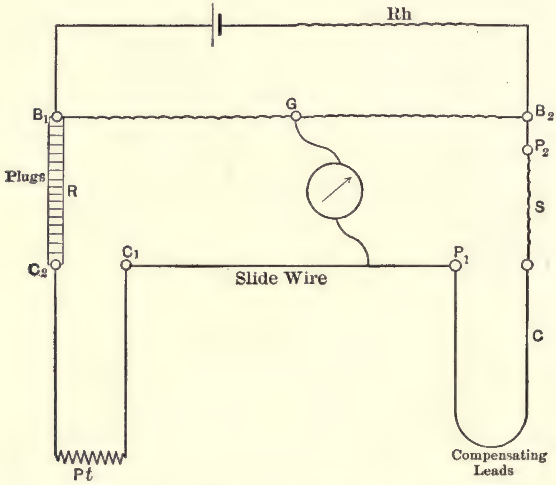


Fig. 138. Circuits for Deflectional Recorder.

The compensator leads are connected in series with the balancing coils. With this arrangement the resistance $S + C$ is nearly constant, so that if the galvanometer deflection is adjusted to be correct when the thermometer is at 0° C., or any convenient temperature, the scale will be very nearly correct when the thermometer is at any other temperature, the plugs R being suitably adjusted. A much greater sensibility can be obtained in this way than with thermocouples using such a recorder. Thus it is possible to get a scale of 50 mm. to 1° C. if desired. Such great sensibility, however, would only be necessary in extremely delicate thermostatic control. The scale of the galvanometer is not strictly one of equal parts, and this has to be allowed for in exact work.

The Leeds and Northrup Recorders. — This firm has developed two types of resistance recorders suitable for temperature measurements, one having an electromagnetic control and the other mechanical. The former has been perfected to a definite instrument and the latter is still undergoing improvement in details. Both are of the balance type and give pen records proportional to temperatures in rectangular coördinates; in both the recording mechanism is entirely independent of the galvanometer system, and the accuracy uninfluenced by changes in the galvanometer constant.

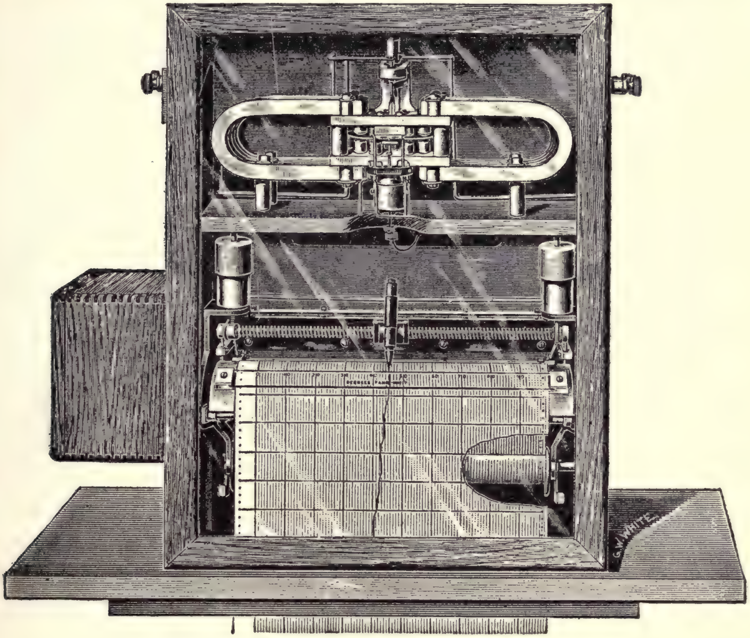


Fig. 139. Leeds and Northrup Recorder.

The general appearance of the recorder with electromagnetic control is shown in Fig. 139. As usually constructed, this recorder is made for any range over 100° F. to 1800° F. with a sensibility of $\frac{1}{5}$ per cent and a constancy of repetition of $\frac{2}{5}$ per cent. The pen will follow temperature changes at the rate of $\frac{1}{5}$ per cent of the total range per second, giving a continuous terraced record.

The complete recorder consists of four essential parts: a differential galvanometer, with a plunger magnet attached to it, for operating periodically the contactor; a clock which drives the paper and operates the contacting plunger magnet; a simple mechanism consisting of a screw and two electromagnets of the plunger type for traveling the pen and the balancing contact; and a paper drive, moved by the clock, which feeds a continuous band of paper off a roll and over an apron carrying it under an ordinary stylographic pen.

The mechanical recorder is of the same general design, except that the moving mechanisms are all driven mechanically, with the added factor that, according as the galvanometer needle is more or less deflected, the pen mechanism will be driven faster or slower. This permits following much more rapid temperature changes than with the electromagnetically controlled recorder.

Both of these instruments may also be arranged for use with thermocouples; and the mechanical recorder has besides been adapted to record directly the differential-temperature curve (page 382) by means of a double galvanometer system, the paper moving proportionally to the temperature of the sample and the pen proportionally to the difference in temperature between the sample and neutral.

Carpentier's Electrothermal Recorder. — This system gives rectilinear coördinates by the use of a cylindrical frame containing the paper, which advances continuously and against which the pen carried by the galvanometer boom impinges periodically by means of the following electrothermal mechanism: The galvanometer boom carries a fine wire of platinum-silver through which an electric current, either direct or alternating, may be sent from an auxiliary, or the ordinary lighting circuit. The recording pen and wire are so attached to the end of the boom by a spring that when no current is passing in the wire the pen is free of the paper; but the passage of a current weakens the tension of the wire, due to its expansion, and the spring then pulls the pen gently against the paper without shock. With a suitable commutator, as many as four contacts per second may be had on the paper; and where several records are to be taken on the same sheet for as many separate thermometers, the same principle of electrothermal control may be applied also to the commutator, giving, when the contact surfaces are so spaced, dots or dashes of different length for each circuit.

This type of recorder and commutator may evidently be used with any kind of pyrometer whose readings may be taken with a galvanometer.

Thermoelectric Recording Pyrometer. — We shall group the thermoelectric recording methods according to the type of curve which they register, — temperature-time, differential, and temperature-rate, — all of which may be realized both with photographic and autographic registering apparatus. Due perhaps to the general convenience of the thermocouple for temperature measurements, there appears until very recently to have been more attention paid to the development of recording methods for this type of pyrometer than for any other, and this in spite of the fact that the thermocouple labors under the disadvantage, as compared with the resistance pyrometer, for instance, in having intrinsically very little energy available for the mechanical operation of a recorder.

It would seem to be mainly for this reason that the early thermoelectric recorders were photographic instruments; and, in fact, it is only in recent years that satisfactory autographic thermoelectric recorders have been devised, and they employ various artifices to maintain the sensitiveness of the registering galvanometer, necessitating usually an intermittent or dotted record, at least with Pt-Rh thermocouples. The difficulty of the problem, in this case, is emphasized when it is recalled that only very weak currents can be had; thus for a precision of 10° C. an apparatus sensible to $\frac{1}{40000}$ volt is necessary, and as the galvanometer should have at least 100 ohms resistance, as previously explained, when the deflection method is used, the corresponding current will be only a millionth of an ampere.

In those cases where it is permissible, as in many industrial measurements, to use certain alloys of the base metals which develop large E.M.F.'s, and whose resistance is so low that the galvanometer resistance may also be reduced, it is possible to realize pen recorders giving a strictly continuous record curve of a precision sufficient for many technical operations.

Temperature-rate Recorders. — As we have seen, it is sometimes of interest, more particularly in the laboratory, to measure directly the speed of the occurrence of certain phenomena, as the rate of cooling or chemical transformation. We require an apparatus that will give the rate of change of temperature of the sample in terms of its temperature.

Le Chatelier's Experiments. — Le Chatelier used this method in 1887 in his study of the properties of clays. He was also the first to employ a photographic apparatus for the recording of cooling- or heating-curve data, using an arrangement, to be described, in which the photographic plate remained stationary.

A luminous beam reflected by the galvanometer mirror falls periodically at regular intervals, of a second for instance, upon a fixed sensitive plate. The distance apart of two successive images gives the variation of temperature during unit time, that is, the rate of heating or of cooling; the distance from the same image to the image corresponding to the beginning of the heating will give the measurement of the temperature.

In all cases of photographic recording it is well to replace the ordinary galvanometer mirrors, which give images quite insufficient as to definition and brightness, by special mirrors made of a plano-convex lens, silvered on the plane surface. These mirrors are slightly heavier than parallel-face mirrors, but have two important advantages: the absence of extra images reflected by the front surface of the mirror, and a greater rigidity, which obviates accidental bendings of the mirror arising from the attachments to its support. One may easily get good mirrors of this type of 20 mm. diameter, and with more difficulty of 30 mm. diameter. These last give nine times more light than the mirrors ordinarily employed. It is easy to so choose the lens as to give a mirror of desired focal length. A plano-convex lens whose principal focus by transmission is 1 m. will give, after silvering the plane surface, an optical system equivalent to a spherical mirror whose radius of curvature would be 1 m.

Le Chatelier used discontinuous recording. In this manner of recording, the luminous source should possess periodic variations; one of the simplest to employ is the electric spark between two metallic points. The interruption of the current is produced by a pendulum at definite intervals of time.

In order to have a spark sufficiently bright, it is necessary to use an induction coil so worked as to give freely sparks of 50 mm., and to reënforce it by a Leyden jar which reduces the length of these sparks to 5 mm.; it suffices for this to use a jar of 1 to 2 liters. The choice of metals for the points is equally important; zinc, aluminium, and especially magnesium give sparks that are very photogenic. These metals possess the disadvantage of oxidizing quite rapidly in the air, so that it is necessary from time to time to clean the points with a file. The metallic sticks may have 5 mm. diameter, and the distance apart of the points is 2 mm. One might without doubt, using mercury, which gives sparks as photogenic as does magnesium, construct an inclosed apparatus in which the metal would be preserved unchanged.

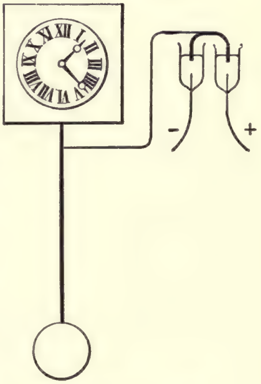


Fig. 140. Clock Interrupter.

To produce the interruption, there is attached to the pendulum (Fig. 140) a vertical platinum fork which dips into two cups of mercury covered with alcohol. It is useful, in order to reduce to a minimum the resistance that the immersion of the fork opposes to the motion of the pendulum, to place this fork in the same horizontal plane as the axis of rotation of the pendulum. In this way one avoids the translatory movements in the mercury which cause the most trouble.

The only refinement with this intermittent lighting is to obtain, with a spark much too large and irregular to be photographed directly, the illumination of a very narrow slit. It is not sufficient to place the spark behind the slit and at a small distance away, because the slightest displacement of the spark would cause the luminous beam to fall outside of the mirror of the galvanometer. This difficulty is overcome by a well-known artifice. A lens is placed between the electrodes and the mirror (Fig. 141); the position of the electrodes is so adjusted that the image of the mirror is formed between them. With a distance apart of the electrodes of 2 mm., a lens of 100 mm. focal length and a mirror of 25 mm. diameter, the image of the latter will touch the two points; the spark then necessarily crosses the image of the mirror, and the radiations passed by the lens will fall certainly upon the mirror. One is thus sure in placing before the lens a fine metallic slit that all the rays transmitted will reach the mirror and will be sent to the photographic plate, and that whatever may be the position of the slit in front of the lens.

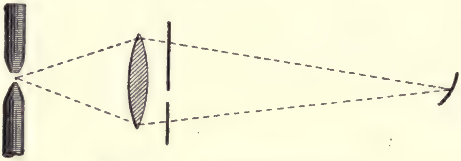


Fig. 141. Focusing Device.

To save time, it is advantageous to take several sets of observations on the same plate; this is easily done by arranging the plate so that it may be displaced vertically between two series, or in adjusting the slit so that it may be moved similarly before the lens.

The diagram (Fig. 142) is the reproduction of negatives relative to the action of heat on clays. The first line gives the graduation of the couple; it has been drawn from several different photographs which have been grouped to economize space. The following lines are reproductions of negatives made photographically without any intervention of the hand of the engraver. The second line, for example, represents the heating of an ordinary clay. A slight contraction of the lines between 150° and 350° indicates a first phenomenon with absorption of heat; it is the vaporization of the inclosed water. A second cooling much more marked between 550° and 650° shows the dehydration, properly so called, of the clay, the liberation of the two molecules of water in combination. Finally, the considerable spacing of the lines at 1000° shows a sudden setting free of heat corresponding to the isomeric change of state, after which the alumina becomes insoluble in acids. The other rows refer to the heating of other varieties of clay, the third row to kaolin, the fifth to steargillite.

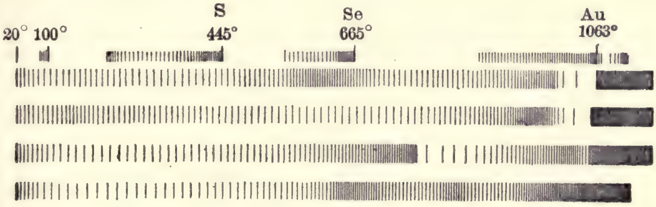


Fig. 142. Heating Curves of Clays.

Dejean's Apparatus. — Another method of recording the rate of heating or cooling in terms of the temperature has been devised by Dejean. The new feature of this method, which gives a continuous record, is the use of an induction galvanometer or relay which may be inserted in the circuit of the more sensitive galvanometer G_1 of the Saladin system (Fig. 160). The principle of the apparatus is shown in Fig. 143. The induction relay is a modified d'Arsonval galvanometer having an electromagnet and a movable coil, the latter consisting of two distinct insulated windings, one of which is connected to a thermocouple. Heating or cooling one junction of this couple causes the coil to be deflected and its motion in the field of the electromagnet induces an E.M.F. in the second winding of the coil which is proportional to its angular speed and hence to the rate of change of E.M.F. of the couple, or approximately to the rate of cooling or heating, i.e., to $\frac{d\theta}{dt}$. The induced E.M.F. is measured by joining this winding to the sensitive galvanometer G_1. The galvanometer deflection passes through a minimum when the heating or cooling passes through a minimum, that is, for a region in which there is an absorption or evolution of heat. A second thermocouple in series with the other galvanometer G_2 of the Saladin system gives the temperature of the sample. We have, therefore, on the plate P (Fig. 134), when the record is taken photographically, the temperatures as abscissæ and the rate of cooling $\frac{d\theta}{dt}$ as ordinates. Dejean has used this method in the study of steels and has also investigated with it the copper-cuprous oxide system. The transition temperatures are very sharply marked. If desired, direct reading may be substituted for the photographic recording, with an increase in precision. Unless the temperature is changing rapidly, however, this method lacks sensitiveness. It is evidently a perfectly general method for recording the rate of change of E.M.F. $\left(\frac{dE}{dt}\right)$.

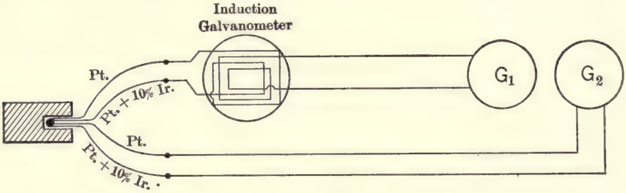


Fig. 143. Dejean's Apparatus.

In neither Le Chatelier's nor Dejean's arrangement can differences in the rate of heating or cooling due to the substance itself be distinguished from those due to external causes, since no neutral piece is used (see page 382).

Temperature Time Recorders.—There have been a great many types of instruments constructed for recording temperatures directly in terms of time for use with thermocouples. The early forms were for the most part photographic, giving continuous records, while many of the more recent ones are autographic, which usually give discontinuous results. We can mention only a few which illustrate sufficiently well the principles involved.

The Apparatus of Sir Roberts-Austen. — On account of its historical interest as well as its intrinsic usefulness, we shall first describe, with some of its modifications, the photographic apparatus of the late Sir Roberts-Austen, director of the royal mint at London.

A vertical slit lighted from a convenient source projects its image, by means of the galvanometer mirror, on a metallic plate pierced by a fine horizontal slit, and behind this slit moves a sensitive surface — plate or paper — which receives the luminous beam, defined by the intersection of the horizontal slit with the image of the vertical slit. If all were at rest, the impression produced by this luminous beam would be reduced to a point. If the plate alone is moved, a vertical straight line will be had; if the galvanometer mirror alone turns, a horizontal line. Finally, the simultaneous displacement of the plate and mirror gives a curve whose abscissæ represent temperatures, and whose ordinates, time. The illumination of the slit and the motion of the sensitive surface may be realized in many different ways.

Regarding the *lighting of the slit*, there are two quite distinct cases to consider, — that of laboratory researches by rapid heating or cooling, which last only a few minutes, and that of continuous recording of temperatures in industrial works, which may last hours and days, that is to say, periods 100 times to 1000 times longer. The rate of displacement of the sensitive surface, and consequently the time of exposure to the luminous action, may vary in the same ratio. The luminous source necessary will be therefore quite different, depending upon the case. For very slow displacements it is sufficient to use a small kerosene lamp with a flame of 5 to 10 mm. high. For more rapid displacements use may be made of an ordinary oil lamp, an Auer burner, or an incandescent lamp; finally, for very rapid displacements of the sensitive plate, 10 mm. to 100 mm. per minute, one may advantageously employ the oxyhydrogen flame or the electric arc. For oxyhydrogen light the most convenient is the lamp of Dr. Roux, with magnesium spheres; it consumes little gas and is inclosed in a metallic box which prevents all troublesome diffusions of the light. In more modern apparatus the Nernst lamp is often used.

The electric arc gives much more light than is needed, and the rapid wearing away of the carbon, by displacing the positions of the luminous point, renders difficult the permanence of suitable illumination of the slit. For very short experiments one may very conveniently use the mercury lamp in vacuo (Fig. 144) or the arc playing between two mercury surfaces. In order to run it, 3 amperes at 30 volts are requisite. Its only disadvantage is its liability to go out after running a few minutes on account of the evaporation of the mercury in the central tube. It suffices, it is true, to give it a slight jar to make it go again, by causing a small quantity of mercury to pass from the outside annular space into the central tube. Special forms of mercury lamp exist, however, which are free from this trouble.

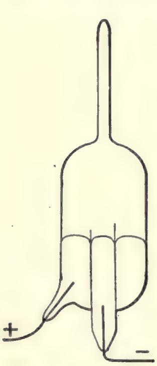


Fig. 144.
Mercury Lamp.

Whatever the luminous source employed, the slit may be always lighted by means of a lens arranged as was indicated for discontinuous recording, that is, projecting upon the galvanometer mirror the image of the luminous source. When this is large enough, it suffices to place the slit before the luminous source, bringing it up close enough so as to be sure that some of the luminous rays, passing through, fall upon the mirror. But there is danger here of so considerably heating the slit that it may be altered; for this reason one is led to use more voluminous light sources than would otherwise be necessary. In the case of the use of a lens, the useful luminous intensity is as great as in placing the slit immediately next to the luminous source, so long as the image of the latter is greater than the galvanometer mirror; now with the ordinary dimensions of the sources employed this condition is always fulfilled without any special precaution.

Instead of a slit lighted by a distinct luminous source, use may be made of a platinum wire, or better, as does Charpy, employ a carbon filament of an incandescent lamp heated by an electric current.

In order that the line traced by the recorder be very fine, it is necessary that the two slits, the luminous slit and the horizontal slit, be equally fine. Skillful mechanicians can cut such slits in metals. But it is easier to make them by taking a photographic plate of bromide gelatine that has been exposed to the light, developing until completely black, then wash and dry. By cutting the gelatine with the point of a penknife guided by a ruler, one may get transparent slits of a perfect fineness and sharpness.

For *sensitive surfaces*, use is made of plates or films of bromide gelatine. Professor Roberts-Austen employed exclusively plates which permit more easily the printing of a great number of positive proofs. Charpy, in his researches on the hardening of steel, made use of sensitive paper, which permits a much more simple installation.

For industrial recording, *paper* would allow of the employing large rolls lasting several days, as in the recording magnetic apparatus of Mascart. But in general one wants to have quickly the results of the record; this is always the case in laboratory investigations, and almost always in industrial studies. It is thus preferable to be content with quite short bands of paper rolled on a cylinder. There exists such a model quite well known and easy to use: the recording cylinders with an interior clock movement of the firm Richard, Paris. They may be ordered from the maker with any desired rate of rotation; unfortunately, this rate cannot be changed at the pleasure of the operator, a desideratum in laboratory investigations.

In the apparatus used by Charpy, or in its very elaborate form as constructed by Toepfer of Potsdam, for Kurnakow, the vertically moving plate is replaced by a rotating cylinder wound with the sensitized paper on which the deflections of the galvanometer are registered. This form of recorder had also been used and discarded by Roberts-Austen. Fig. 145 represents the installation of the recording pyrometer used by Charpy in his researches on the quenching of steel. To the right is the galvanometer, to the left the Richard recording cylinder, and in the middle the electric furnace used for heating the samples of steel. It is interesting to note in passing that Charpy was the first to use electric heating in this kind of work. Kurnakow's apparatus, which must be placed in a dark room, is furnished with an auxiliary telescope and scale system using red light, so that the experiment may be controlled during the taking of a record. As constructed, five speeds may be given to the cylinder; and there is provided an E.M.F. compensating system for maintaining the maximum sensibility over a series of temperature ranges.

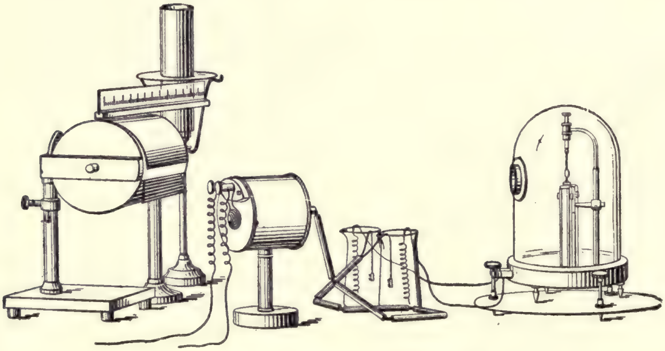


Fig. 145. Charpy's Apparatus.

There is another device, used by C. L. A. Schmidt, by which the experiment may be watched while a photographic record of a cooling curve is being taken. It consists in shunting the sensitive photo-recording galvanometer G (Fig. 146), in series with a high resistance R, across a direct-reading millivoltmeter V. If the resistance of $R + G$ is great compared with that of V, the readings of the millivoltmeter will not be altered appreciably by this operation. Schmidt moves the photographic plate, mounted as in the apparatus of Roberts-Austen, by means of a screw driven by a small motor. In this way any desired speed may be given to the plate.

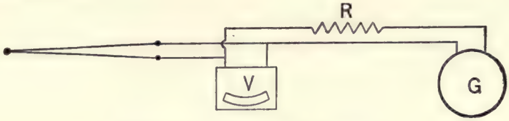


Fig. 146. Schmidt's Device.

If *plates* are used, they may be placed in a movable frame regulated by a clock movement; this is the first arrangement employed by Professor Roberts-Austen (Fig. 147). But this installation, somewhat costly and complicated, has the same disadvantage as the recording cylinders, in that but a single speed can be given to the sensitive surface. In order to drive the plate,

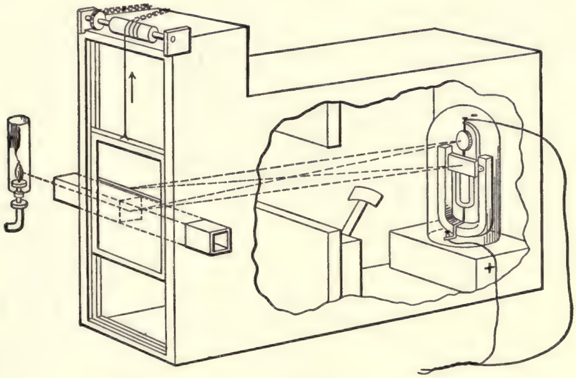


Fig. 147. Apparatus of Roberts-Austen.

Roberts-Austen later used a buoyed system in which the rate of rise of level of the water is controlled at will by the agency of a Mariotte's flask and a simple water cock. The plate is kept in an invariable vertical plane by means of two lateral cleats whose friction is negligible on account of the mobility of the float. The sketch (Fig. 148) gives the arrangement of a similar apparatus made by Pellin for the laboratory of the Collège de France. It carries a 13 by 18 cm. plate which is attached to the float by means of two lateral springs not shown in the sketch. Neither are the two guides of the float, immersed in water, indicated; the play next the cleats is only two-tenths of a millimeter. The uncertainty that this play can cause in the position of the plate is quite negligible. The curve (Fig. 149) is the reproduction of an experiment made with such an arrangement by Roberts-Austen on the solidification of gold.

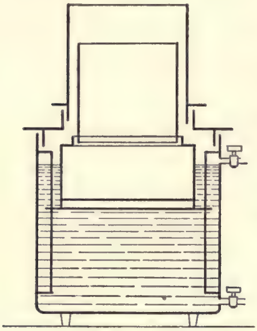


Fig. 148. Plate-holder.

During the whole period of freezing the temperature remained stationary, then lowering of temperature was produced at a regularly decreasing rate as the temperature of the metal approached that of the surroundings.

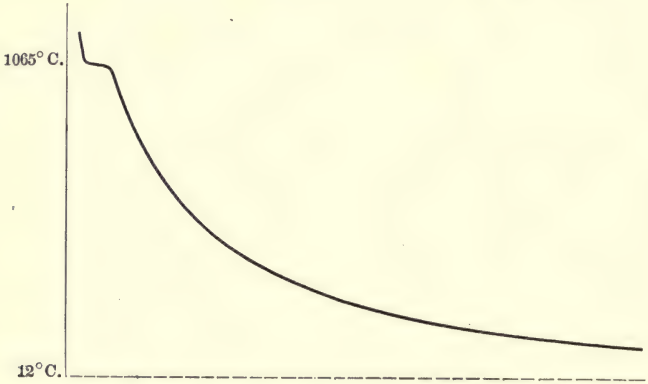


Fig. 149. Record with Apparatus of Roberts-Austen.

It is indispensable to trace, on each sensitive surface on which is to be recorded a curve, the line corresponding to the surrounding temperature, or at least a parallel reference line. This is very easy in the case of the guided plate or of the paper rolled on a cylinder. It suffices, after having brought the couple to the temperature of its surroundings, to displace in the opposite direction the sensitive surface; the second curve traced during this inverse movement is precisely the line of the zero of the graduation of the temperatures. But this is a dependence that may be evaded by registering at the same time as the curve a reference line by means of a fixed mirror attached to the galvanometer in the path of the luminous beam which lights the movable mirror. Roberts-Austen likewise made use of the luminous beam reflected by the fixed mirror to inscribe the time in a precise manner. A movable screen driven by a second pendulum cuts off at equal intervals of time this second luminous beam. The reference line, instead of being continuous, is made up of a series of discontinuous marks whose successively corresponding parts are at intervals of one second, as is shown in Fig. 149.

The curves once obtained must be very carefully examined to recognize the points where the gradient presents slight anomalies, characteristic of the transformations of the body studied. Generally these irregularities are very insignificant, and it would be well, in order to recognize them with certainty, to obtain curves traced on a much greater scale. Practically this magnification is not possible without auxiliary devices which limit either the range or the sensibility; thus the sensitiveness of the galvanometer may be increased, and so the deflection, but then for the greater range of temperature the luminous image would fall off the sensitive plate.

In practice it has been found difficult to realize conveniently a sufficiently steady motion of the plate in the Roberts-Austen system of recording, and attempts have been made to devise methods in which the photographic plate remains fixed in position. This has been successfully accomplished by Saladin, whose apparatus (Fig. 160, page 419) has been modified by Wologdine to give the temperature-time curve by removing the prism M and substituting for the second galvanometer G_2 a plane mirror turning about an horizontal axis. This mirror may be controlled by an hydraulic system as in Roberts-Austen's apparatus, or by clockwork as in the model constructed by Pellin of Paris. The deflection of the galvanometer G_1 gives to the beam of light an horizontal motion over the plate proportional to the temperature, while the vertical motion of the beam of light is given by the mirror turning at a uniform rate, and is therefore approximately proportional to the time as registered on a flat plate.

Autographic Recorders. — To obtain a satisfactory autographic or pen record with platinum thermocouples without sacrifice of sensibility of the galvanometer, it is necessary to eliminate the friction of the pen or stylus upon the paper. This has been accomplished by the use of mechanisms which cause the pen or stylus at the end of the galvanometer boom to make only momentary contact with the moving paper.*

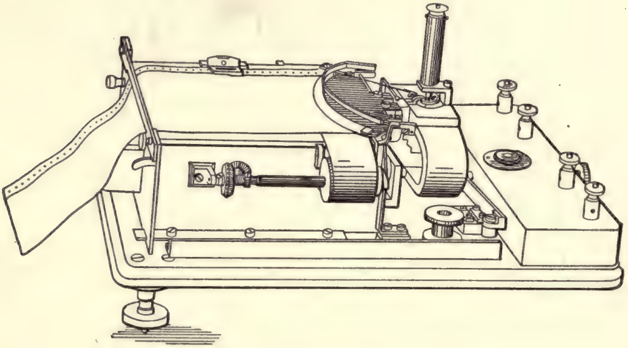


Fig. 150. Siemens and Halske Recorder.

In the Siemens and Halske form of instrument (Figs. 150 and 151), the paper *P* is driven forward by the same clockwork that controls the pressing down, by means of the arm *B*, of the stylus *N*, which imprints dots periodically on the paper by means of a typewriter ribbon running across and beneath the record sheet. This system permits of taking a record continuously over very long periods of time. In most of the other recorders the paper is wound upon a drum, and various devices are used to obtain the record; thus in the Hartmann and Braun type a silver stylus makes sulphide dots on a prepared paper, and in the Cambridge thread recorder rectangular coördinates are obtained by having the galvanometer boom strike an inked thread which runs parallel to the drum (Fig. 152).

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* There are a considerable number of thermoelectric recorders. Among the manufacturers of these instruments are: Siemens and Halske, Berlin; Hartmann and Braun, Frankfort a. M.; Pellin, Chauvin and Arnoux, Carpentier, and Richard, Paris; Leeds and Northrup, the Thwing Instrument Company, and Queen of Philadelphia; the Scientific Instrument Company of Cambridge, England, and Rochester, N. Y.; the Bristol Company, Waterbury, Conn.

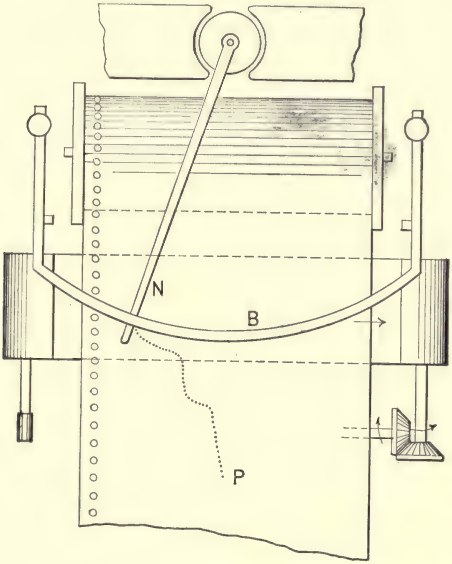


Fig. 151. Principle of Recorder.

A Siemens and Halske drum recorder with pivot galvanometer, suitable for technical work, and which is inclosed in a dustproof metallic case, is shown in Fig. 153. It may be adjusted for seven-day records.

As previously stated, these autographic instruments all give intermittent records for the platinum thermocouples, and are limited to one or two speeds; and although they may be made very sensitive they are not adapted for the detection of transformations which take place very rapidly, since the recording

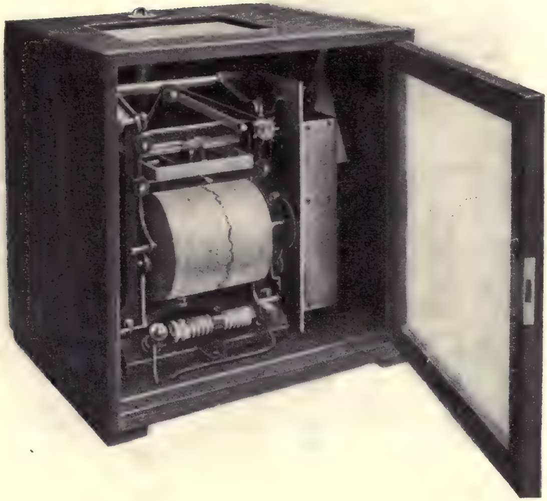


Fig. 152. Thread Recorder.

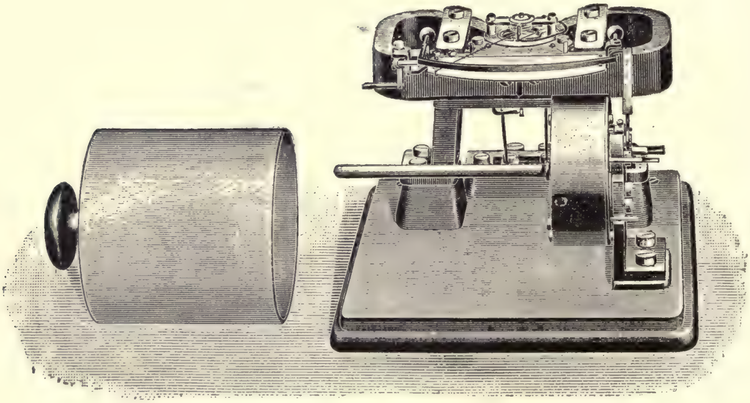


Fig. 153. Drum Recorder.

interval cannot readily be shortened much below 10 seconds, and in most instruments this interval is greater than 15 seconds. In other words, they can be used advantageously only for slow cooling or heating.

A continuous pen record may be obtained with galvanometers suited for use with the base-metal couples developing high E.M.F.'s, such as the Bristol, Hoskins, Thwing, etc.

In order to eliminate the effect of irregularity of outside conditions which influence the rate of cooling, a method commonly used when endeavoring to detect small transformations consists in placing a second thermocouple in the furnace, but sufficiently removed from the substance studied to be uninfluenced by its behavior. Alternate readings on the temperature of the test piece (θ) and of the furnace (θ') are then taken, preferably at definite time intervals. The data are most readily discussed by plotting the two temperature-time curves side by side as shown in Fig. 154, or by plotting the difference in temperature $\theta - \theta'$ against the temperature θ of the test piece.

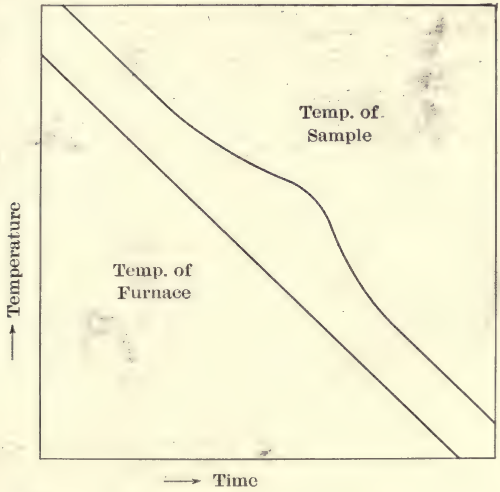


Fig. 154. Furnace and Charge Temperature Curves.

This method may be made recording either by using two instruments or by modifying one of the above-mentioned autographic recorders so as to trace the curves of two thermocouples on the same sheet. In practice, however, this method is usually resorted to only when great sensibility is desired, as in detecting minute internal-energy changes, when the potentiometer combined with the deflection galvanometer is the most sensitive and quick-working arrangement for taking the measurements. It is convenient to use thermocouples of the same composition so as to have readings of both the temperature of the sample and of the furnace given by the same potentiometer setting, and so depend upon the galvanometer deflections for measuring the residual parts of θ and θ'.

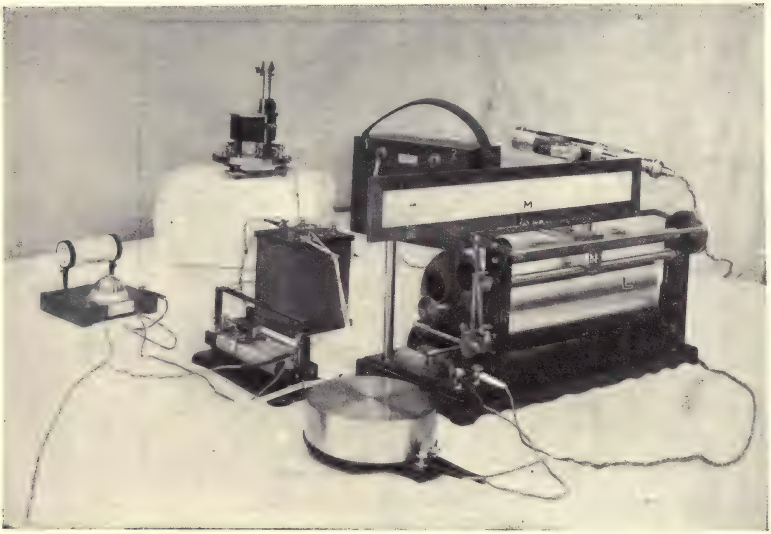


Fig. 155. Brearley Curve Tracer and Accessories.

Regarding the precision of this method, it is to be noted that the quantity it is really desired to measure is $\theta - \theta'$ in terms of θ, and this is accomplished by measuring θ and θ', hence the sensibility of $\theta - \theta'$ is no greater than that of θ or θ'. In other words, the method requires the maximum refinement of measurement to obtain the quantity sought, as well as the maximum of computation or plotting to reduce the observations.

Semi-automatic Recording. — The Brearley curve tracer, manufactured by the Cambridge Company, is a semi-automatic apparatus for registering the time-temperature curve. As shown with accessories in Fig. 155, a small tube furnace is connected to an electric supply main so as to heat the specimen within the furnace; a platinum-iridium couple, whose hot junction is within the specimen, is connected in series with a resistance and moving coil galvanometer of adjustable sensibility; a Nernst lamp furnishes illumination and gives a sharp image at *M* on the scale *G*. The rotating drum *L* is surmounted by a sliding carriage *N* carrying two pointers, one of which, *M*, is fixed, and the second, immediately below, carries a pen and is depressed every second on the paper wound on the drum. The pointer *M* is made to follow the spot of light by the operator by turning a handle at the end of a long screw on which *N* runs. There is electromagnetic clock control of the drum and of the pen. The record is therefore a series of dots one second apart. The temperature scale may be made as open as desired, and a complete heating and cooling curve for a steel sample may be obtained in a few minutes. This instru-

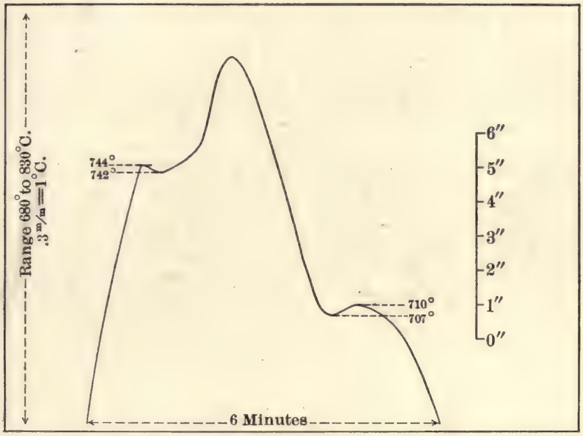


Fig. 156. Curves with Brearley Apparatus.

ment is also now made to give a continuous record. A sample curve is shown in Fig. 156.

Another method of working, in which the apparatus is completely autographic for relatively short temperature intervals, and at the same time very sensitive, is to use a recording galvanometer in connection with a potentiometer. This requires the operator to adjust the dials of the potentiometer to step from one temperature interval to the next, these intervals varying in length with the galvanometer sensibility, which should be capable of adjustment to give longer or shorter temperature intervals.

Differential Curves. — The method of page 411 may readily be modified so as to give $\theta - \theta'$, the difference in temperature between the test piece and furnace, by direct measurement instead of by computation, with the added advantage that the precision of $\theta - \theta'$ may be made very great as compared with that of θ, the temperature of the sample. This may be accomplished, for example, by placing a commutator, which may be driven by a clock mechanism, in the thermocouple circuit at *A*, Fig. 157, so that alternate measurements on θ and $\theta - \theta'$ may be taken in terms of the time. Evidently the connections may be made so that either the galvanometer G_2 of the same direct-reading or potentiometer system that measures θ, or a separate instrument G_1, as shown in the figure, may be used to measure $\theta - \theta'$. Both galvanometers may be photographic or autographic recorders.

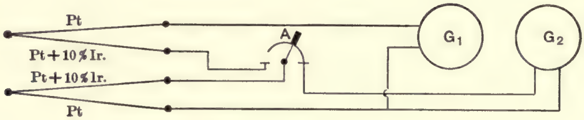


Fig. 157. Method of Burgess.

Use of a Neutral Body. — Accidental variations in the indications of the auxiliary thermocouple giving θ', the furnace temperature, may largely be eliminated by placing this couple within a blank or neutral substance. The material of the neutral body should be such that it undergoes no transformations involving an absorption or evolution of heat within the temperature range studied, such as a piece of platinum, porcelain, or even in some cases nickel or nickel steel. It is also desirable that the sample and neutral have as near as may be the same heat capacities and emissivities. The sample to be studied and the neutral piece are placed near together and arranged symmetrically with respect to the temperature distribution within the furnace.

To Roberts-Austen again was due the credit of first devising a sensitive differential method using the neutral body. He also modified his photographic recorder (Fig. 147) so as to give, by means of a second galvanometer, the $\theta - \theta'$ *vs* t curve on the same plate with the θ *vs* t curve, from which a curve giving $\theta - \theta'$ in terms of θ could be constructed. His arrangement of the direct-reading and differential thermocouple and galvanometer circuits is shown in Fig. 158 in which S is the sample or test piece, and N the neutral body possessing no transformations; the galvanometer G_2 measures the temperature θ of the sample, and G_1 measures the difference in temperature $\theta - \theta'$ between the sample and the neutral. Curves for steels and alloys were usually taken with the samples in vacuo.

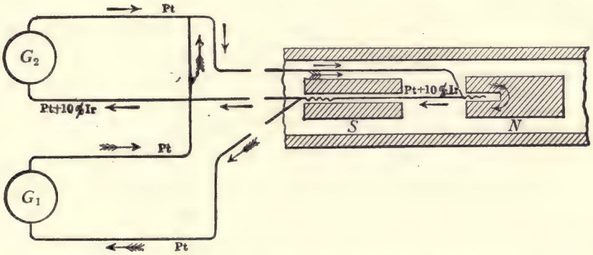


Fig. 158. Use of Neutral, Roberts-Austen.

It is evident that Roberts-Austen's final photographic apparatus, although very sensitive, was also complicated and very delicate of adjustment, and in practice it took great skill in its use, requiring for instance some three or four successive exposures adjusted to the proper adjacent temperature ranges, to take the cooling curve of a steel from 1100° to 200° C.

Most of the recent exact work employing the principle of this method has been done by taking the observations of θ directly on a potentiometer and $\theta - \theta'$ on the same or an auxiliary galvanometer. In this case of direct reading, the simpler arrangement of thermocouples indicated in Fig. 157, due to Burgess, may advantageously replace Roberts-Austen's (Fig. 158), or the modification shown in Fig. 159, such as used by Carpenter and others. The first dispenses with one thermocouple and the drilling of a second hole in the sample.

This method is evidently capable of attaining maximum sensitiveness, since the galvanometer connected to the differential thermocouple, giving $\theta - \theta'$ *vs* t, may be made as sensitive as desired independently of the θ *vs* t system. There is the further advantage that no limits are set to the range of temperatures over which a given precision in $\theta - \theta'$ may be had. There is, however, a limitation on the certainty of interpretation of results by this method, especially when the rate of cooling is rapid, due to the fact that it is practically impossible to realize the ideal condition of having $\theta - \theta'$ = a constant, or keeping the cooling curves of the test piece and neutral parallel for temperature intervals within which there are no transformations of the test piece. The rate of cooling, and hence the value of $\theta - \theta'$, is influenced by several factors, among the most important of which are the mass of each substance, — the unknown and the neutral, — its specific heat, conductivity, and emissivity, as well as the relative heat capacities of the furnace and inclosed samples. The $\theta - \theta'$ *vs* t

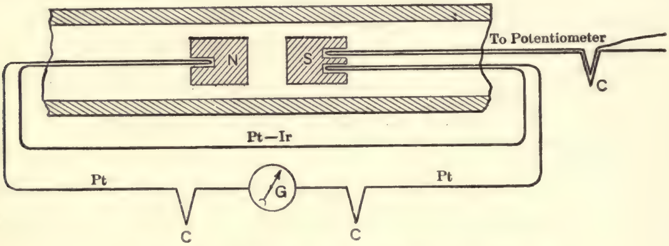


Fig. 159. Arrangement used by Carpenter.

line is, however, always a smooth curve, except for the regions in which there are transformations in the substance under study.

The autographic system of recording may also be used, and it is possible to construct an apparatus by means of which both the θ *vs* t and $\theta - \theta'$ *vs* t curves shall be recorded simultaneously on the same sheet by the same galvanometer boom. In order to accomplish this, we have made use of a Siemens and Halske recording millivoltmeter having a total range of 1.5 millivolts and a resistance of 10.6 ohms. The E.M.F. generated by the differential thermocouple, proportional to $\theta - \theta'$, is recorded directly by this instrument. 1° C. corresponds to from 16 to 19 microvolts between 300° and 1100° C. for a platinum-iridium couple, or to about 1.8 mm. on the record paper. In series with the Pt-Ir thermocouple giving temperatures is a suitable resistance, about 200 ohms in this case, so that the galvanometer boom may be kept within the limits of the paper when recording values of θ. The circuit is made alternately through the direct and the differential thermocouple circuits in series with the recorder by means of a polarized relay actuated by the same battery that depresses the galvanometer boom when the mark is made on the paper. The thermocouple circuits may be those of either Figs. 157, 158, or 159, but with the galvanometer G_2 indicating temperatures suppressed.

It is evident that by recording the two curves, $\theta - \theta'$ *vs* t and θ *vs* t, on the same sheet there is some sacrifice in the ability to detect small and rapid transformations, since the spacing is doubled. Usually also, with such an arrangement, the galvanometer will not be completely aperiodic for one or the other system. On the other hand, it is of great advantage to have the curves together and obtained independently of inequalities in clock rates, which are a serious source of error in locating transformation points exactly when two separate instruments are used. The same result may be effected by shunting the galvanometer when on the temperature side. This of course cuts down very greatly the resistance of the thermocouple circuit, a disadvantage unless a sensitive galvanometer of high resistance is used. Such galvanometers suitable for mechanical recording are not yet available. In Thwing's recording pyrometer, two galvanometers, one giving temperatures and the other differences, impress their records on a single chart driven by one clock.

When it is desired merely to detect the existence of a transformation without measuring its temperature exactly, the sensitive form of recording millivoltmeter may be connected directly to the differential thermocouple without other accessories, as was done by Hoffmann and Rothe in studying the transformations of liquid sulphur.

Saladin's Apparatus. — It is sometimes of advantage to be able to record and discuss the data independently of the time, and so express $\theta - \theta'$, the difference in temperature between sample and neutral, directly in terms of θ, the temperature of the sample. This may evidently be accomplished by replotting the results obtained from the curves of the previous differential methods which involve the time. It was reserved, however, to Saladin, engineer of the Creusot Works, to invent, in 1903, a method that would record photographically the θ *vs* $\theta - \theta'$ curve directly, thus obviating any replotting. His method possesses also the advantage of having the photographic plate fixed in place. The forms of curve obtained in this way are illustrated in Fig. 134.

The arrangement of the apparatus in its simplest form, due to Le Chatelier, is shown in Fig. 160. Light from the source S strikes the mirror of the sensitive galvanometer G_1 whose deflections measure the differences in temperature $(\theta - \theta')$ between the sample under study and the neutral body. The horizontal deflections of the beam of light are now turned into a vertical plane by passing through the totally reflecting prism M placed at an angle of 45 degrees. A second galvanometer G_2, whose deflections are a measure of the temperature of the sample and whose mirror in its zero position is at right angles to that of G_1, reflects the beam horizontally upon the plate at P. The spot of light has thus impressed upon it two motions at right angles to each other, giving, therefore, on the plate a curve whose abscissæ are approximately proportional to the temperature θ of the sample and whose ordinates are proportional to $\theta - \theta'$. The sensitiveness of the method depends upon that of the galvanometer G_1, which may readily be made to give 5 or 6 mm. for each degree centigrade. The arrangement of the thermocouple circuits is the same as in Figs. 158 or 159. If so desired, the time may also be recorded by means of a toothed wheel driven by a clock and placed in the path of the beam of light. Compact forms of this apparatus, which is used considerably in metallurgical labora-

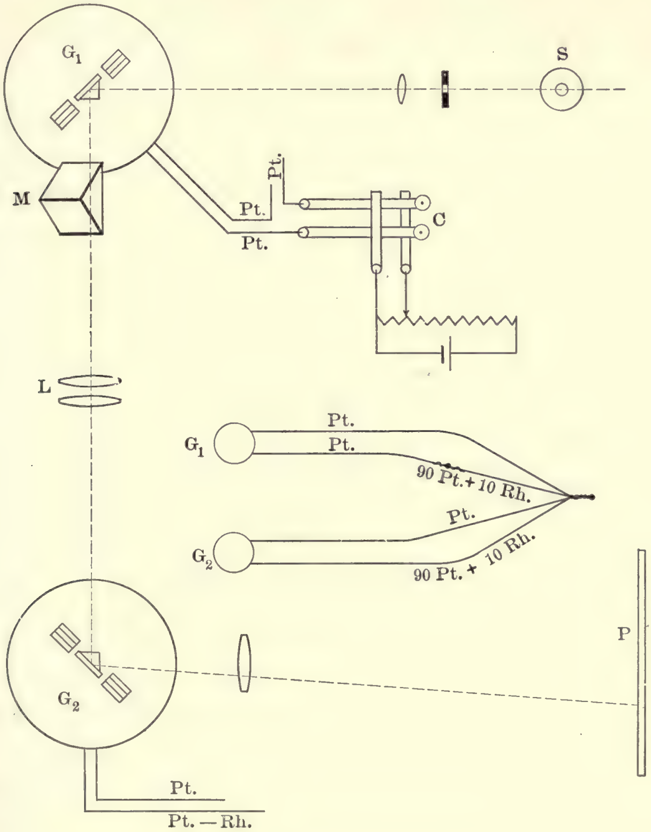


Fig. 160. Saladin's Apparatus.

tories, are made by Pellin, Paris, and by Siemens and Halske, Berlin. The lens between G_1 and G_2 may be suppressed.

When steels and metallic alloys in the solid state are being investigated, advantage may be taken of the thermoelectric behavior of the sample itself to record the critical regions with Saladin's apparatus. Thus Boudouard measures $\theta - \theta'$ by means of platinum wires set into crevices at each end of the sample, taking advantage of the fact that the transformation will usually be progressive along the sample. This modification eliminates the neutral piece and one platinum or alloy wire, but, as Le Chatelier has shown, is less accurate than the usual form of Saladin's apparatus; and its indications may even be indeterminate or ambiguous, as the reaction may start midway between the embedded wires or at either end.

Saladin's method, it should be noted, is a perfectly general one for recording the relations between any two phenomena which may be measured in terms of E.M.F. or as the deflections of two galvanometers. The Leeds and Northrup Company have recently modified their autographic recorder, p. 393, to trace the θ *vs* $\theta - \theta'$ curve, using several differential couples in series in order to obtain the required sensibility.

Registration of Rapid Cooling. — None of the experimental arrangements so far described is adapted for measuring the very rapid cooling, i.e., several hundred degrees in a few seconds, met with in such processes as quenching or chilling. The development of methods for measuring rapidly varying temperatures will undoubtedly be of great use in the solution of many physical and metallurgical problems involving products whose properties depend on cooling velocities. Only a few preliminary investigations into this field, however, have as yet been made.

Le Chatelier's Experiments. — Le Chatelier, in an investigation of the quenching of small samples of steel, and the effect of various baths, made use of a galvanometer having a period of 0.2 second and a resistance of 7 ohms, whose deflections, produced by the current from a thermocouple inserted into the specimen undergoing the quenching, were recorded on a photographic plate moving vertically at a speed of 3 mm. per second. A half-second's pendulum vibrating across the path of the beam of light, from a Nernst glower as source, gave a measure of the time. He succeeded in recording satisfactorily temperature intervals of 700° C. in 6 seconds, using as samples cylinders 18 mm. on a side, and obtained results of great interest to the theory and practice of hardening steel samples by quenching in baths of various kinds of liquids. Le Chatelier recognized the desirability of increasing the precision and sensitiveness, and of improving the technique, of this method, and suggested the advantages of using for the registration an oscillograph arrangement, or a string galvanometer of very short period such as Enithoven's, in which the displacements of a silvered quartz fiber of high resistance in an intense magnetic field are measured photographically.

Benedicks' Experiments. — Following the suggestions of Le Chatelier, Benedicks has carried out a series of researches on the cooling power of liquids, on quenching velocities, and on certain constituents of steel. The errors in cooling curves of metals have also been studied recently by Hayes.

Benedicks' apparatus, as arranged for taking the time-temperature curve of steel samples during quenching, is shown in Fig. 161. The principles here applied may evidently be used in other kinds of experimentation involving rapid cooling.

The specimen *A* is heated in a small electric furnace *B*, which is provided, in its lower part, with a narrow opening parallel to the longitudinal axis, through which passes a holder *C*, which turns about an horizontal axis, being given a definite torque by a spiral spring *D*, and maintained vertical by an electromagnetic control *E*. Through a bore in *C* a thermocouple is led into the interior of *A*, and the cold junction is contained in the ice box *F*, from which the wires are led to a commutator *G* by means of which either the thermocouple *A* or the calibrating apparatus *b*, *c*, etc., may be connected to the measuring instrument *J*, this being a small string galvanometer by Edelmann of Munich. The light from the arc lamp *K*, passing through the microscope of the galvanometer, fitted with a projection eyepiece, gives an image of the movable string on the registration apparatus *L*, provided with a rotating cylinder which carries the sensitive paper.

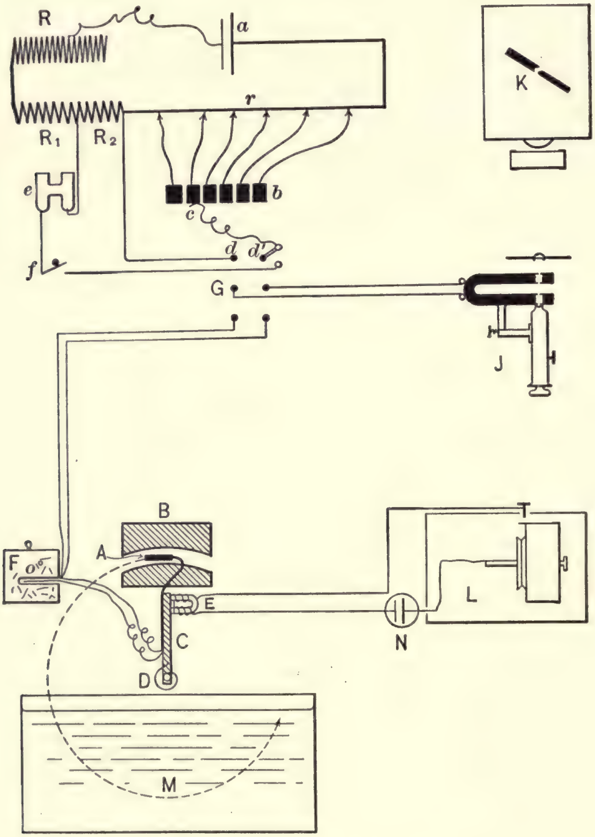


Fig. 161. Apparatus of Benedicks.

Finally, the electromagnet release *E* is connected with an accumulator *N* and a contact *T* on the shutter before the cylinder *L*.

The process of registration is therefore as follows: The cylinder *L* is set in rotation, and as the edge of the sensitive paper passes the window *T* the shutter rises. At the same instant the circuit of *E* is closed, releasing the arm *C*. This automatically and quickly quenches the specimen *A* in the cistern of water *M* beneath.

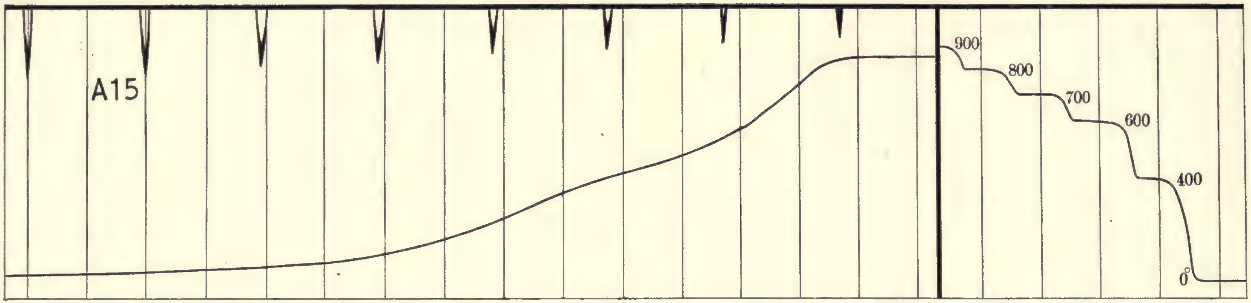
Precautions have to be taken in insulating the thermocouple wires leading into the specimen and in insuring good contact of the couple junction against the specimen with a water-tight joint. Capillary tubes of fused quartz, which will also stand sudden temperature changes, were used for insulating, and water was prevented from entering joints by means of compressed air introduced into the containing tube *C* of the thermocouple wires.

The calibrating apparatus consists of a sliding commutator *c*, *b*, the blocks of which are connected to fixed points on a slide wire *r* in such positions as to give electromotive forces corresponding to definite temperatures, 400°, 600°, etc., of the thermocouple when the resistances R, R_1, and R_2 are properly adjusted; variations in the battery *a* are controlled by the standard cell and resistance *R*. This arrangement allows calibrating the galvanometer immediately before each experiment and give the calibration data on the same sheet as the quenching curve.

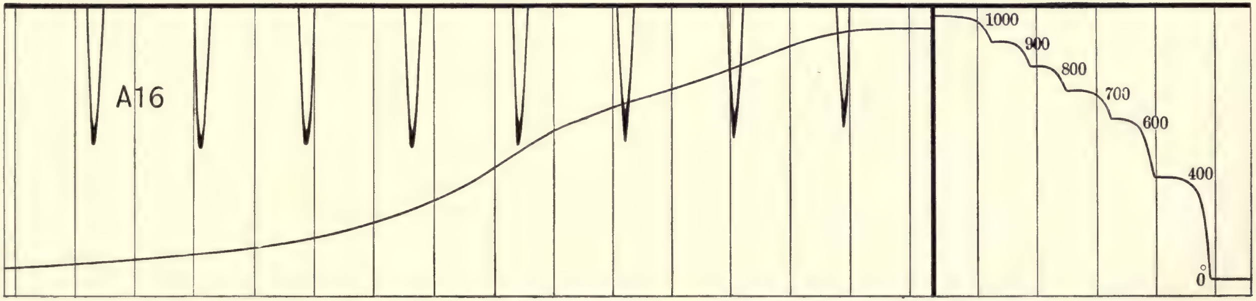
The string galvanometer had a resistance of 6700 ohms; its sensitiveness may be adjusted to follow that of the thermocouple, although this is not necessary. The time correction of this galvanometer is such, fortunately, that the directly registered curve is simply a parallel curve to the one which would be obtained if the deflections were absolutely instantaneous; or in other words, no correction for the inability of the instrument to respond instantaneously is necessary. There remains, of course, a small unknown time correction due to the lag of the thermocouple with respect to the test specimen.

In Fig. 162 are shown curves for a steel of 0.42 carbon quenched both from 850° and 950° C.; the time τ is taken to 100° C. The calibration curves are also shown in the figure.

Recording Radiation Pyrometers. — Any phenomenon whose magnitude may be measured by the deflection of a galvanometer may be rendered self-registering by optical means. Total or



Carbon, 0.42 per cent; quenched at 850°→15°; mass, 12.3 grammes; $\tau = 3.60$ seconds.



Carbon, 0.42 per cent; quenched at 949°→15°; mass, 12.4 grammes; $\tau = 4.63$ seconds.

Fig. 162. Quenching Curves with Benedicks' Apparatus.

monochromatic radiation falling on the exposed strip of a bolometer may, therefore, be made to record its intensity, which is, as we have seen, a function of the temperature of the radiating body. Langley, in 1892, rendered his bolometer a recording instrument, the records being taken photographically. This system of recording has been used mainly for the mapping of solar spectra, and incidentally for the estimation of the sun's temperature and in other astrophysical investigations; and although it might be used in laboratory investigations in recording high temperatures in terms of either total or monochromatic radiation, it has not come into any general use for such purposes. The experimental arrangements are necessarily very elaborate and delicate, for descriptions of which the reader should consult the Annals of the Astrophysical Observatory of the Smithsonian Institution. Callendar has applied also his slide-wire method of recording electrical resistances to Langley's bolometer. The curve of Fig. 163 gives the record of solar radiation for a day.

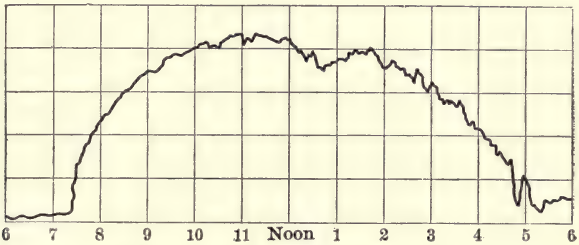


Fig. 163. Solar Radiation Record.

The radiation pyrometers of the Féry type are readily made self-registering, it being only necessary to substitute for the indicating galvanometer a suitable deflection-recording instrument, such as the Cambridge thread recorder or a Siemens and Halske recording millivoltmeter of the required range and sensitiveness. In Fig. 164 is shown the record of the temperature of a pottery " biscuit " kiln as taken with a Féry radiation pyrometer and Cambridge thread recorder. A Callendar slide-wire recorder could also be used to register very high temperatures if too great sensitiveness be not demanded.

The Morse or Holborn and Kurlbaum instruments may be made semi-recording; that is, a registering ammeter may be put in the lamp circuit and made to record each temperature to which the pyrometer is set by the observer. This method would have some advantages in the control of those industrial operations for which this type of pyrometer is best adapted.

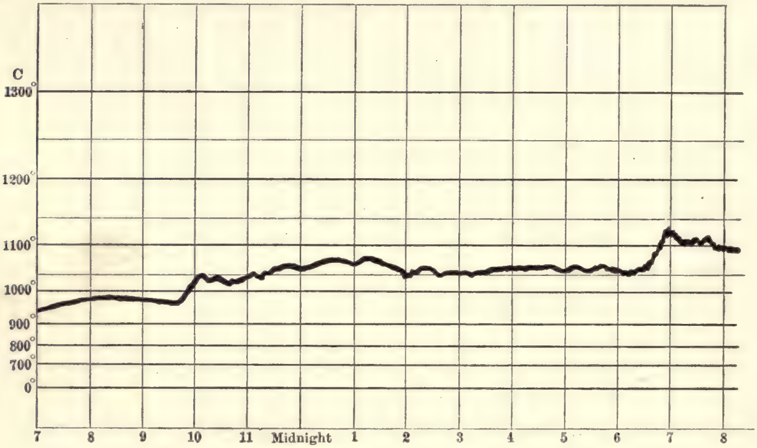


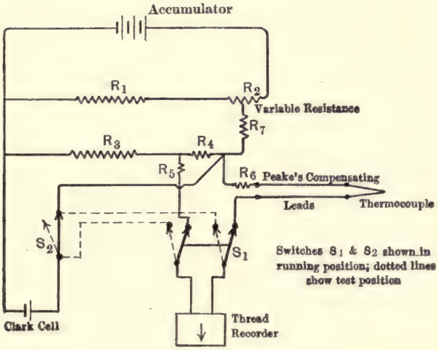
Fig. 164. Temperature Record of Pottery Kiln.

Recording Accessories. — We may mention, finally, a number of auxiliary pieces of apparatus and methods which are useful in special cases.

Range Control. — It is sometimes desirable to limit the range of the recorder to some restricted temperature interval and thereby gain greater sensibility with a more open temperature scale. This may be done in several ways. We shall use as illustrations the scale-control box of Peake as applied by the Cambridge Company to their thread recorder. In its more complete form this device is shown in Fig. 165, for use with thermocouples provided with Peake's compensating leads (page 176).

A 6-volt accumulator passes a current through a series of fixed resistances, R_3, R_4, R_7, and a portion of a variable resistance R_2, the potentiometer circuit.

A second circuit, the pyrometer circuit, consisting of the couple, leads, R_6 and R_5, and the recorder, is connected to tap onto the ends of the coil R_4 in the potentiometer circuit. Thus the potential drop in R_4, due to the current from the accumulator, is opposed to the electromotive force of the couple, and, therefore, at some particular temperature, say 750° C., the two just balance, and no current will flow through the pyrometer circuit. If now the temperature of the couple falls, a current will flow in one direction through the recorder, whilst if it rises a current will flow in the reverse direction. Thus the zero or undeflected position of the recorder pointer may be made in the center of the scale, and will correspond in the above case to 750° C., whilst the resistance R_5 may be so adjusted that one end of the scale will correspond to 600° C., and the other to 900° C.



Switches S1 & S2 shown in running position; dotted lines show test position

Fig. 165. Peake's Scale Control Box.

The accuracy of the arrangement depends upon the current in R_4 being maintained constant, and to secure this a Clark cell is connected across the resistances R_3 and R_4. When the accumulator voltage is normal, this cell does not give any current, but if accumulator voltage falls slightly, the Clark cell gives a slight current and tends to keep the voltage across the terminals of R_3 and R_4 nearly constant.

The change in E.M.F. of the Clark cell with temperature also balances very nearly the corresponding changes in the compensating leads, so that the behavior of the apparatus is nearly independent of cold-junction temperature fluctuations. The arrangement may be simplified but rendered less exact by dispensing with the Clark cell.

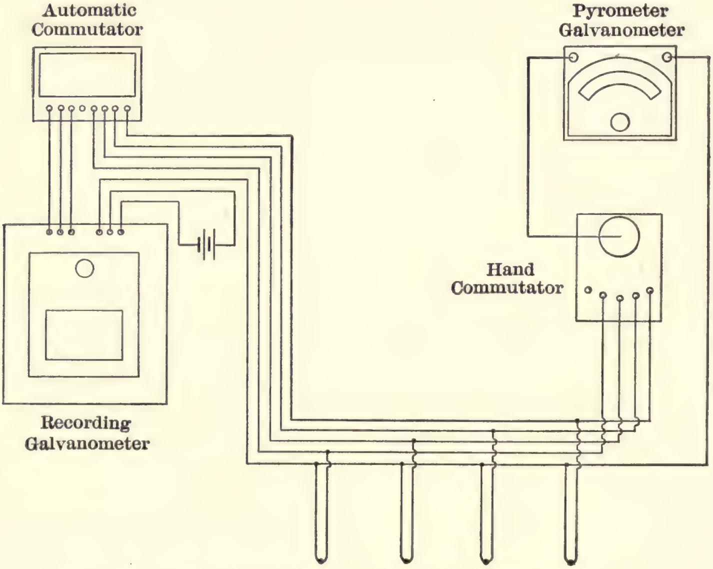


Fig. 166. Recorder and Indicator with Four Thermocouples.

Multiple Records and Circuits. — There are various devices for taking several records on a single sheet by means of one galvanometer. They practically all reduce to some type of automatically driven commutator and are often so constructed that the several records may be distinguished by the spacing or length of dots and dashes. While it is proper to record simultaneously quite different temperatures, it is usually good practice not to try and so record temperatures that frequently overlap on the sheet, as its interpretation may then become doubtful. It is also often convenient to have on one circuit a recorder, which may be in an office, together with one or more indicating instruments. An arrangement of four thermocouple circuits is shown in Fig. 166, whereby a recorder gives a continuous record for all the couples, and the temperature reading of each of them may also be taken by means of an indicating galvanometer.

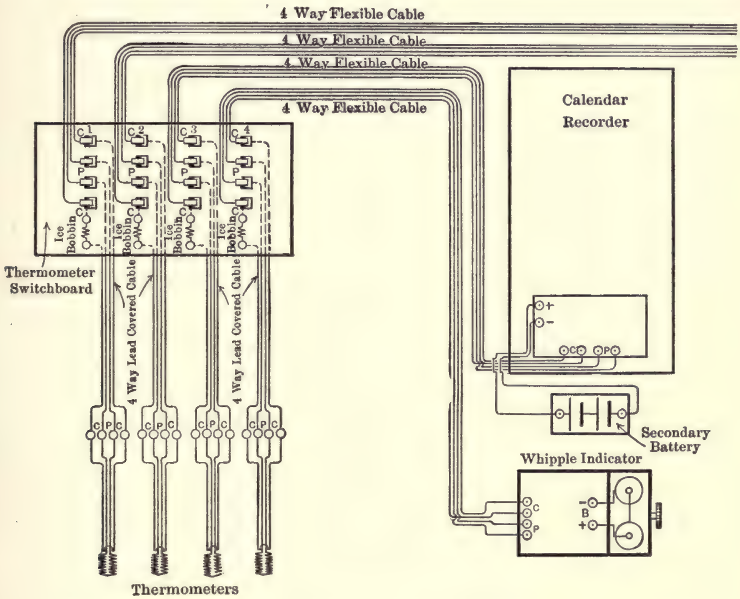


Fig. 167. Recorder and Indicator with Four Resistance Pyrometers.

A switchboard may also be used permitting interchangeability of pyrometers, as illustrated in Fig. 167, where four resistance-thermometer circuits are provided for, to be used with various instruments as required. See also Fig. 70.

In general, it may be said that almost any industrial requirement of combination of pyrometer circuits, recording and indicating instruments and alarms may be solved satisfactorily in practice.

Furnace Control and Thermostats. — In certain operations, — for example, in taking heating and cooling curves, — it is advantageous to raise or lower the temperature of the electric furnace continuously at a uniform rate. This is readily accomplished for an alternate-current supply by the use of a salt-water rheostat fed on heating from a Mariotte bottle. The metal electrodes may be cut to shape to favor the uniformity of rise in temperature; during the cooling the water is siphoned off. The whole apparatus may be made completely automatic, if desired, so that a series of heating and cooling curves may be taken at any desired rate without the intervention of the observer. It is well to keep the temperature of the rheostat down by circulating water through it in a coil of pipe.

It is often desirable to maintain a furnace at constant temperature. The method used will depend largely upon the temperature in question.

In the range over which liquid baths may be used, to 350° C. with suitable oils, they are satisfactory when properly stirred and provided with thermostatic control. With a sensitive gas regulator a constancy of 0.05° C. may be maintained, and with electric control a somewhat better uniformity.

A uniform temperature over a large volume may be established by means of a vapor in equilibrium with its liquid. This system is not available for high temperatures, and it is difficult to maintain a constant temperature over long periods of time.

For high temperatures air baths only can be employed, the most usual form being the electric resistance tube furnace. Special windings and delicate control are required if it is desired to maintain a considerable volume at constant temperature. Various devices have been suggested for the automatic control of furnace temperatures, based usually on the use of relays actuated either electrically or optically. Most of the recorders we have described may be fitted with such an accessory.

We may also cite the optical regulator of Kolowrat which will keep an electric furnace constant to 2° or 3° at 1000° C., and may be applied to either thermoelectric or resistance measurement of temperature. The light from a powerful source, a Nernst lamp, is reflected from the galvanometer mirror onto a scale representing temperatures. When in adjustment an increase in temperature of the furnace throws the spot of light onto a thermopile which operates a series of relays cutting in resistance to the heating circuit and cooling the furnace slightly. This resistance is cut out when the spot leaves the thermopile.

Among the many electric thermostatic controls we may mention that of H. Darwin, which may also be used as an alarm (Fig. 168). When the galvanometer needle *GV* is deflected from the stop *V*, due to a rise in temperature, the needle engages the wheel *W* driven by clockwork and makes a circuit at *L*, which may be either that of an alarm, as shown, or that of a regulating circuit by means of relays.

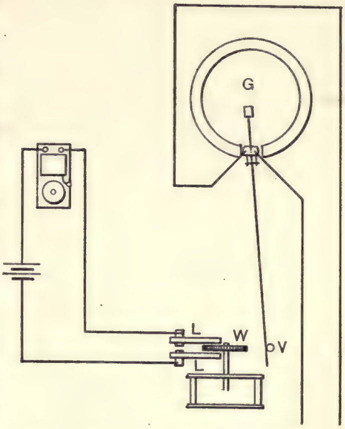


Fig. 168. Darwin Temperature Alarm.

CHAPTER XI.

STANDARDIZATION OF PYROMETERS.

Thermometric Scales. — The generally recognized standard temperature scale is that of the gas thermometer, which, as we have seen, has been realized in the form of the constant-volume nitrogen thermometer to 1550° C. This scale is fixed by the determination of certain reference temperatures, such as melting or freezing and boiling points. It would be desirable to define temperatures in terms of the normal or thermodynamic scale, which is independent of the properties of any particular substance. At the present time, however, the limit of accuracy attained in gas pyrometry does not exceed the departure of the constant-volume gas scale from the thermodynamic scale; and the scale as defined by various gases is also practically identical, so that for most practical purposes we may speak in terms of either scale interchangeably.

Above the range of the gas thermometer, we are compelled to resort to extrapolation in terms of some phenomenon varying with the temperature. For this purpose, use is usually made of the radiation laws based on the relations which have been found to exist at lower temperatures between the intensity of total and monochromatic radiation and temperature. Just as the thermodynamic scale of temperature is independent of the thermal properties of any particular substance, but would be reproduced exactly by an ideal gas, and is very nearly realized by the thermal properties of ordinary gases: similarly, the radiation scale of temperature is independent of the radiating properties of any particular substance, but would be reproduced exactly by the radiation from a black body, and is very nearly realized by the radiation from an almost completely closed, clear furnace at a uniform temperature. The radiation scale, then, may be, and in practice is, so defined as to be the thermodynamic scale, so that we have in reality a single, continuous-temperature scale from the lowest to the highest attainable temperatures.

Unfortunately, there is not as yet a sufficiently good agreement among the few temperatures above 1200° C. determined with the gas thermometer, so that there is still considerable uncertainty in the values to assign to the constants in the radiation laws and therefore to fixed points in the higher ranges.

Fixed Points. — As the scale determined by the gas thermometer is the one universally recognized, it is necessary, in order to calibrate a pyrometer, to express its indications in terms of the gas scale. In general, it is not feasible to compare the readings of a pyrometer directly with those of the gas thermometer. The use of the latter becomes restricted mainly to the establishment of certain constant, reproducible temperatures or fixed points such as are given by freezing points and boiling points of the chemical elements and of certain compounds. The accuracy attainable in pyrometric researches is, therefore, limited by the exactness of our knowledge of these reference temperatures, and their determination has been and still is of the most fundamental importance in pyrometry. There have been a great many temperatures suggested for this use, but the actual number available is very small. Preference should, in general, be given to those determinations made with the gas thermometer itself, although there are others made indirectly in terms of the gas scale, as with thermocouples, optical pyrometers, and resistance thermometers, which are of considerable weight; and in fact the more common practice, when working with the gas thermometer, is to compare its readings in a furnace or bath with those of some more convenient instrument and then transfer the gas scale by means of the latter to the melting or boiling points by interpolation.

We have already called attention to many of these determinations of fixed points, among which the following may be considered in greater detail:

Sulphur.—(Boiling) *444.6°* C. on the constant-volume scale of nitrogen, or *444.5°* on the constant-pressure scale; corresponding to about 444.7° on the thermodynamic scale, under a pressure of 760 mm.; with a variation of 0.090° per millimeter change of mercury in the atmospheric pressure.

The boiling point of sulphur has been the object of several series of distinct observations, among which we may cite the following, distinguishing between direct and strictly independent determinations with the gas thermometer and indirect ones by italicizing the former.

BOILING POINT OF SULPHUR.

Observers.	Method and remarks.	S.B.P. observed.	Corr. to const. vol. $p_0=1$ at.
Regnault	Const. vol., about	*447.5°*	....
Crafts	Const. vol.	*445*	....
Callendar and Griffiths	Const. press.	*444.53*	*444.74°*
Reichsanstalt	Const. vol. Wiebe and Bötcher scale	444.5	444.5
Chappuis and Harker	Const. vol. corr. from 445.2°	*444.7*	*444.7*
Holborn	Const. vol. extrapolated Pt. resistance	444.55	444.55
Rothe	Const. vol. Hg thermo. P.T.R. scale	444.7	444.8
	Thermocouples	445.0	....
Eumorfopoulos	Const. press.	*444.55*	*444.76*
Holborn and Henning	Const. vol.	*444.51*	*444.51*
	Best value from above series		***444.6***

Regnault's figure was obtained by plunging the reservoir of the thermometer in the liquid sulphur; but this liquid will superheat, and so gives too high a value. The other eight very concordant results were obtained in the vapor.

The result first published by Chappuis and Harker, using a constant-volume thermometer, was 445.2°, but this difference from Callendar and Griffiths' result was shown probably to be due mainly to an incorrect value assumed for the expansion coefficient of the porcelain bulbs used by the former. Eumorfopoulos first published the value 443.7°, which was recognized at the time to be uncertain, as it depended upon the unknown expansion coefficient of mercury, which has since been determined by Callendar and Moss to high temperatures.

Callendar and Griffiths as well as Eumorfopoulos worked with a constant-pressure air thermometer, and it is of interest to note that the outstanding difference between several of the experimental determinations by the constant-volume and constant-pressure methods is of the order of difference to be expected between the two gas scales, — constant-volume and constant-pressure, — as seen from Callendar's table (page 31) and from Fig. 1. In fact, in work of the highest precision it will probably soon be desirable to reduce observations to the thermodynamic scale.

At the Reichsanstalt a new determination of the S.B.P. has recently been carried out by Holborn and Henning, using several gases and bulbs of glass and quartz. Their result is about 0.2° C. lower than would be expected from the measurements at constant pressure.

In order to reproduce the exact value of the sulphur boiling point, however, it is not sufficient to plunge the protected thermometer into the sulphur vapor, but it is necessary to guard it against superheating by radiation from the liquid and lower walls, on the one hand, and cooling by liquid sulphur condensed on the thermometer case and radiation from the thermometer, on the other hand. Unless proper precautions are taken, variations of 1° C. may be found. Sulphur boils very smoothly without bumping, and, in a properly constructed apparatus, condenses in a very sharp line near the top of the boiling tube. A conical or cylindrical aluminium shield with an umbrella cap fitting close about the thermometer stem serves the double purpose of shielding the instrument from radiation and condensed sulphur. A sulphur boiling apparatus with the protected thermometer in place is shown in Fig. 169, with which measurements consistent to about 0.03° may be obtained. Gas or electric heating may be used, and the boiling tubes may be of hard glass, porcelain, or aluminium. A study by Waidner and Burgess of the various forms of sulphur apparatus used by previous experimenters showed that they give the same temperature to a few hundredths of a degree. Commercial sulphur gives the same boiling point

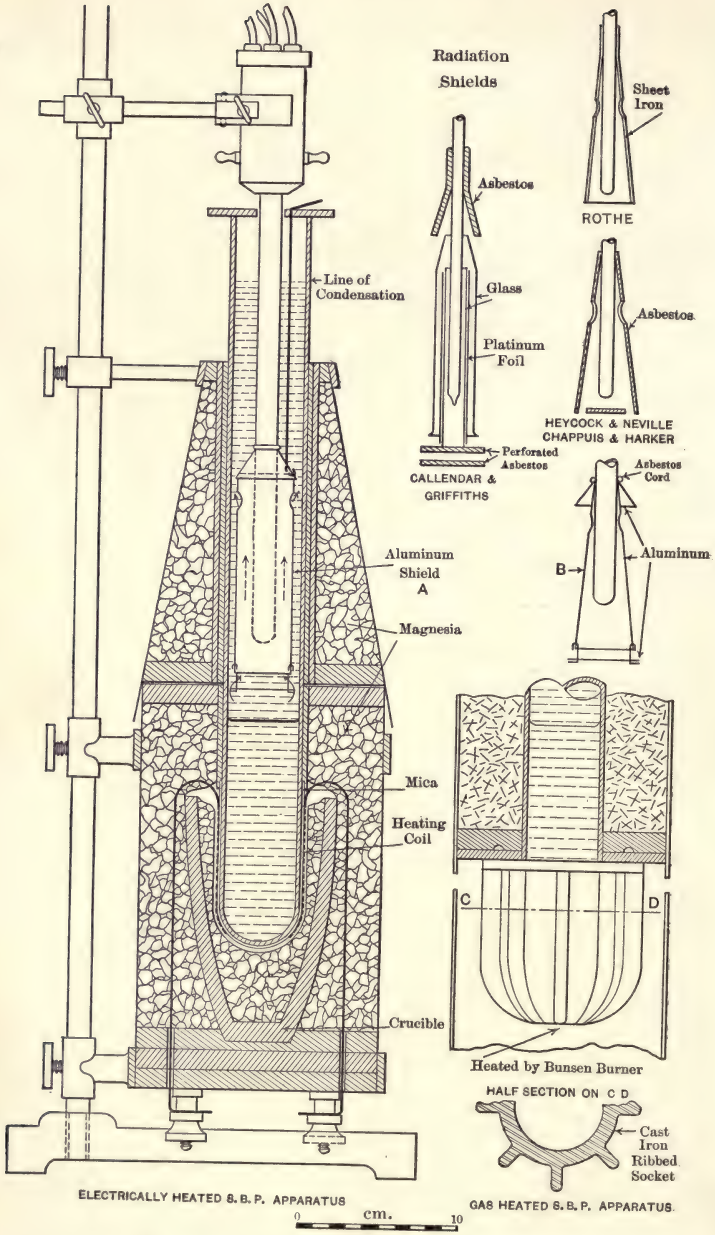


Fig. 169. Types of Sulphur Boiling Apparatus.

as the best sulphur obtainable. A criterium of satisfactory realization of the S.B.P. is the constancy of reading when a thermometer with accessories is displaced several centimeters in the vapor. Waidner and Burgess have also shown that, measured in this way, the column of vapor above boiling sulphur is constant to about 0.03° C.

In spite of the most excellent agreement of the observations in the above table, the determinations with the hydrogen thermometer by Jaquerod and Wassmer of the boiling points of naphthalene and benzophenone, and those by Day and Sosman with the nitrogen thermometer of the freezing points of zinc and cadmium, are not consistent with the value cited above for sulphur. As shown by Waidner and Burgess, using the platinum thermometer, the sulphur point as quoted would be nearly one degree too high in terms of the work of the observers mentioned above. In view of the almost universal use of the sulphur point as a calibration temperature, it is of prime importance to finally fix its value to at least better than 0.1° C.

The several determinations of the change of boiling point of sulphur with pressure are in very close agreement. For exact work, the two-term formula of Holborn and Henning, or that of Harker and Sexton, is to be preferred.

$$t = t_{760} + 0.091_2\,(H - 760) - 0.0_44_2\,(H - 760)^2.$$

Zinc. — (Freezing or melting) *419.4*° C. Freezing points undergo unappreciable changes with variations in atmospheric pressure, and their experimental determination is somewhat easier than for boiling points if a thermocouple is used. The direct determination of a metallic freezing or melting point with a gas thermometer is beset with almost insurmountable experimental difficulties, so recourse is always had to some auxiliary pyrometer whose indications have been exactly calibrated by direct comparisons with a gas thermometer.

Zinc is easily obtained in sufficient purity. Some recent determinations of this point are:

Heycock and Neville	419.4°*
Stansfield	418.2
Holborn and Day	*419.0*
Day and Sosman	*418.2*
Waidner and Burgess	419.37
Holborn and Henning	*419.40*

The first and next to the last values were obtained with the resistance pyrometer, assuming the value for the S.B.P., 444.70°; Stansfield's observation was obtained with a recording thermocouple, and the other is by direct transfer with thermocouples or resistance thermometers from the nitrogen-gas thermometer.

Zinc.—(Boiling) *920*° C., with a variation of 0.15° for a change of 1 mm. in the atmospheric pressure.

The boiling point of zinc has been the object of a great many determinations, and yet it is one of the least known and consequently the most unreliable to try to use, and is not to be recommended. It has been the object of so much study, undoubtedly, as it was apparently the one point near the upper limit of the early experiments with the gas thermometer which could be determined directly by this instrument; but superheating effects in vapors at such high temperatures and an uneven temperature distribution are very difficult to obviate even with electrical heating.

Some of the results obtained are shown by the following table:

E. Becquerel	*930*° and *890*° C.
Sainte-Claire-Deville	*915* to *945*
Barus	*926* and *931*
Violle	*930*
Holborn and Day (two observations)	*910* and *930*
Callendar	916
D. Berthelot	*918*

The value 930° as given by Voille's and Barus' results was generally accepted until recently, but the more recent determinations indicate 930 to be over 10° high. The value adopted, 920°, is probably not in error by over 5° C.

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* The value 419.0° is obtained if an observation on an admittedly too small sample be included.

Gold. — (Fusion or freezing) *1063*° C. This point is to-day one of the best-known fixed points, and gold possesses the advantages of being obtainable in very great purity, is not oxidizable in air, nor is it readily attacked by the silicious materials used in crucibles. Its cost is its only drawback for use in considerable quantities, but methods have been devised, as inserting a short length of wire between the leads of a thermocouple, requiring only very minute amounts of gold. These wire methods give on the average the same results as the crucible method, as shown by Holborn and Day and by D. Berthelot, although their precision is slightly less.

The early determinations of the gold point were quite discordant, but the later ones where electric heating was employed are in excellent agreement.

Pouillet	*1180*° C.
E. Becquerel	*1092* and *1037*
Violle	*1045*
Holborn and Wien	*1070* to *1075*
Heycock and Neville	1062
D. Berthelot	*1064*
Holborn and Day	*1064*
Jaquerod and Perrot	*1067*
Day and Sosman	*1062*

Violle's value was long quoted as the best for the gold point, but the later determinations show it to be some 20° low. Holborn and Wien's high value was obtained with a porcelain-bulb thermometer and is to be considered as replaced by Holborn and Day's value, to obtain which nitrogen in a Pt-Ir bulb was used, together with a thermocouple. The agreement of their results when working under various conditions is shown from the following observations:

Gold, sample 1	1064.0 ± 0.6	(crucible method)
Gold, sample 2	1063.5	(crucible method)
Gold, sample 2	1063.9	(wire method)

Not less than 300 grams was used for observations in both graphite and porcelain crucibles, while by the wire method 0.03 gram of the metal suffices.

Berthelot used his optical gas pyrometer in connection with thermocouples and considers his result to be in error by less than 2 degrees. Heycock and Neville's result was obtained by extrapolation above the sulphur point of the platinum-resistance formula, while Jaquerod and Perrot's value was obtained in terms of a quartz-bulb constant-volume thermometer filled with various gases, the results agreeing to a few tenths of a degree. They used a modified form of the wire method, which consisted in making a small piece of gold wire a part of an alternating electric circuit, melting of the gold being noted by cessation of sound in a telephone.

Day and Sosman used their nitrogen thermometer previously described. A preliminary determination with the same apparatus by Day and Clement gave 1059° for the gold point on a sample found subsequently to contain iron. It was unfortunate that Holborn and Valentiner, in their gas-thermometer work to 1600° C., did not repeat the gold point. An examination of their thermoelectric data shows a discrepancy of about 5 degrees at this temperature from the value here cited as most probable.

Berthelot has called attention to the fact that the later determinations are sufficiently concordant to warrant reducing them to the thermodynamic scale (see page 26).

Observers.	Gas.	Initial pressure.	Corrections.	Observed temp.	Thermodynamic temp.
D. Berthelot	Air	76 cm.	+ 1.36° C.	*1064°*	1065.6°
Holborn and Day	N	29 cm.	0.27	*1064*	1064.3
Jaquerod and Perrot	Air, N O, CO	23 cm.	0.21	*1067.2*	1067.4
Day and Sosman	N	21 cm.	0.21	*1062.4*	1062.6

Silver. — (Freezing or melting) *961.0°*. The freezing point of silver is not a constant temperature except in a reducing atmosphere, and this metal is volatile, thus making it unsafe to use under conditions in which its vapors may attack platinum wires, as of a thermocouple whose electric properties silver alters very considerably.

Many determinations of this point have been made, but it is only the recent observations that take into account the effects of oxidizing and reducing atmospheres. Some of the determinations of the silver point follow:

	Pure Ag.	In air.
Pouillet	.....	*1000*° C.
E. Becquerel	.....	*960* and *916*
Violle	.....	*954*
Holborn and Wien	*970*	...
Heycock and Neville	960.5	955
D. Berthelot	*962*	957
Holborn and Day	*961.5*	955
Day and Sosman	*960.0*	...
Waidner and Burgess	960.9	953 to 957

Melted silver exposed to the air gradually absorbs oxygen, which lowers the freezing point, and this latter is not a definite temperature, varying with the rate of cooling, mass, and surroundings. This lowering may reach 20 degrees or more. The wire method gave 953.6 ± 0.9 as found by Holborn and Day. The freezing point of *pure* silver may be obtained in a graphite crucible in an atmosphere of nitrogen or of CO, or covered with powdered graphite, i.e., in conditions preventing oxidation. The melting or freezing point is equally sharp, and on account of the ease of getting very pure silver its use is strongly recommended as a fixed point.

Copper. — (Freezing or melting) *1063*° in air, *1083*° pure. Whether the gold or the copper point was the higher was long an open question in pyrometry. The great advantage in practice of copper is its cheapness, but the fact that copper apparently has two freezing points does not possess the same disadvantages as with silver, for both of the copper points are very definite, the higher one, 1083°, being that of the pure metal, easiest obtained with a graphite crucible, the metal being protected from the air by a layer of powdered graphite. The lower value, 1063°, is given by the wire method, and copper may replace gold in this way. Values intermediate between 1063° and 1083° will be obtained in crucibles for incomplete protection from air, the effect being due to the formation and solution of cuprous oxide, saturation of the copper with the oxide giving the eutectic point 1063° for about 3.5 per cent Cu_2O. The presence of the eutectic temperature will usually be detectable, whatever the percentage of Cu_2O present, and this fact may be used to check the purity of copper in a crucible.

We may note the following determinations of the copper point:

Heycock and Neville	1080.5°
Stansfield	1083
Holman	1086
Holborn and Day	*1084.1*
Day and Sosman	*1082.6*
Waidner and Burgess	1083

The values obtained by Holborn and Day, and by Day and Sosman, are the only ones determined directly in terms of the gas thermometer. The difference of 20° C. between the Cu and Cu-Cu_2O points has been determined by various observers.

Palladium. — (Fusion) 1550°. This temperature marks the present upper limit of the gas thermometer. The following are some of the recent determinations of the palladium melting point:

Observers.	Method.	Observed melting point.	Reduced to $c_2 = 14{,}500$.
Nernst and v. Wartenberg	Optical; Wien's law, $c_2 = 14{,}600$	1541°	1546°
Waidner and Burgess	Optical; Wien's law, $c_2 = 14{,}500$	1546	1546
Holborn and Valentiner	Nitrogen gas, thermocouples, and optical $c_2 = 14{,}200$	*1575*	1560
Day and Sosman	Nitrogen gas and thermocouples	*1549*	....

Palladium may be melted in air by the wire method and therefore is a convenient control temperature for thermocouples. (See p. 186.) It will be noted that the gas-thermometer determination of Day and Sosman appears to be equivalent to a value of $c_2 = 14{,}450$ in the Wien equation.

Platinum. — (Fusion) 1755°. Above the palladium point, resort must be had to extrapolation. There have been a great many experimental estimates made of the platinum melting point, some of them based only on extrapolation of purely empirical formulæ from temperatures below 1100° C. Such, for instance, are the thermoelectric estimates based on the formula $E = -a + bt + ct^2$ on data which satisfy this equation only in the range 300° to 1200° C. In view of the great importance of this temperature as the best one for reference in the upper part of the scale, all the determinations of which we are aware that have been made are included in the table. The values found prior to the year 1900 are in terms of incorrect values of the basal temperatures, and cannot therefore be correct except by accident.

EXPERIMENTAL DETERMINATIONS OF THE MELTING POINT OF PLATINUM.

Date.	Observers.	Method.	Published melting point.	Reduced to common scale.*
1877–1879	Violle	Calorimetric	1775–1779	....
1892	Barus	Thermoelectric	1757–1855	....
1895	Holborn and Wien	Thermoelectric	1780	....
1896	Holman, Lawrence and Barr	Thermoelectric	1760	....
1898	Petavel	Total light from Pt	1766	....
1903	Nernst	Total light from black body	1782	....
1905	Holborn and Henning	Thermoelectric and optical	1729	....
1905	Holborn and Henning	Thermoelectric	1710	1755
1905	Harker	Thermoelectric	1710	1755
1906	Nernst and Wartenberg	Optical; Wien's law ($c_2=14{,}600$)	1745	1751
1907	Waidner and Burgess	Optical; Wien's law ($c_2=14{,}500$)	1753	1753
1907	Holborn and Valentiner	Optical; Wien's law ($c_2=14{,}200$)	1782	1763
1907	Waidner and Burgess	Monochromatic radiation from Pt	1750	1750
1907	Waidner and Burgess	Thermoelectric (two formulæ)	1706–1730	1753
1909	Féry	Monochromatic radiation from Pt:		
		Oxidizing atmos.	1690	....
		Reducing atmos.	1740	....
1910	Sosman	Thermoelectric from Pd=1549°	1752	1755
1910	Ruff	Optical	about 1750	
		Best Value		**1755**

* This scale is that for which $c_2=14{,}500$ in Wien's law III, p. 251.

The published thermoelectric determinations involving extrapolation on the thermoelectric scale (equation (3), page 112) from low temperatures have little or no weight. The method used by Nernst in 1903 is not capable of great accuracy. Féry's as well as Ruff's measurements appear to have been crude, and the differences noted by the former may be due to the surface properties of the platinum in the different parts of a gas flame and not to the oxidizing and reducing atmospheres as such. All the optical measurements by the other observers were taken in an oxidizing atmosphere and are at least 50 degrees higher than Féry's oxidizing-atmosphere values. The outstanding uncertainty of the platinum point is mainly attributable to the difference assigned to c_2 in the Wien formula and to the different gas scales in terms of which the extrapolations are made. The value here assigned to the platinum point, 1755, is in terms of the Day and Sosman gas scale (Pd = 1549), the optical determinations of Nernst and v. Wartenburg, and Waidner and Burgess, and the mean differences between the palladium and platinum points as found by them and by Holborn and Valentiner, thus:

Observers.	Pt-Pd.
Nernst and v. Wartenberg	204° C.
Holborn and Valentiner	207
Waidner and Burgess	207

Rhodium. — (Fusion) 1940°. The other members of the platinum group have had their melting points less well determined than palladium and platinum. For rhodium the following estimates, among others, have been made:

Mendenhall and Ingersoll (Pt = 1755)	1932
V. Wartenberg (using a tungsten furnace)	1940

Iridium. — (Fusion) 2300°. Although it is questionable if temperature of 2000° C. and over can be determined in terms of the gas scale, it may, nevertheless, be found desirable to determine as exactly as may be one or more fixed temperatures in this range by other methods, as specific heat and the laws of radiation. Iridium and tungsten seem to be the most suitable for this purpose. Hardly any limit of accuracy can as yet be placed upon such determinations. For iridium the following values have been found:

Violle	1950° C.
Veder Weyde	2200
Nernst	2200 to 2240
Rasch (computed from Nernst's data)	2285
Mendenhall and Ingersoll	2300
v. Wartenberg	2360

V. Wartenberg's determination was made in a tungsten furnace in vacuo; that of Mendenhall and Ingersoll of a bead on a Nernst glower.

The recent development of furnaces suitable for use at these extreme temperatures will undoubtedly enable us to more sharply define other points in this part of the scale.

It is interesting to note that at the extreme temperature of the electric arc, 3600° C., the various radiation methods and the specific-heat method give results agreeing to about 100° C.

Other metals melting below 1100° C., such as *cadmium*, *lead*, *antimony*, and *aluminium*, have also been used in the attempt to determine fixed points, and some of the results are given in the accompanying table for metals melting below 1100° C.

TABLE OF FREEZING POINTS TO 1100° C.

Observers....	Stansfield.	D. Berthelot.	Heycock and Neville. Callendar.	Waidner and Burgess	Holborn and Day.	Day and Sosman.
Date..........	1898	1898–1901	1895–99	1910	1900–1901	1910
Instrument...	Recording thermo-couple.	Optical interference.	Electrical resistance.	Electrical resistance.	Nitrogen ther. and thermo-couple.	Nitrogen ther. and thermo-couple.
Calibration data.....	0° 100 444.53	Expansion of air.	0° 100 444.53	0° 100 444.70	Pt-Ir-bulb nitrogen thermometer	Pt-Rh-bulb nitrogen thermometer
Sn.........	232.1°	....	231.9°	231.9°	....	....
Bi.........	268.4	....	269.2	....	....	....
Cd.........	....	....	320.7	321.0	321.7°	320.0°
Pb.........	325.9	....	327.7	327.4	326.9	....
Zn.........	418.2	....	419.0	419.4	419.0	418.2
Sb.........	....	....	629.5	630.7	630.6	629.2
Al.........	649.2	....	645.5	658.0	657.0	658.0
Ag_3–Cu_2...	....	....	778.5	779.2	....	....
Ag (in air).	....	....	955.0	....	955.0	....
Ag (pure)..	961.5	962	960.7	960.9	961.5	960.0
Au.........	1062.7	1064	1061.7	....	1064.0	1062.4
Cu-Cu_2O...	....	....	....	1063.2	1064.9	....
Cu.........	1083.0	....	1080.5	1083.0	1084.1	1082.6

The Iron Group. — A fixed point that has been frequently used is the melting point of nickel (1450°). The thermoelectric determinations based on empirical formulæ gave values varying from 1484 to 1427. Day and Sosman find *1452* with the gas thermometer, and Ruer 1451 with the thermocouple, assuming palladium = 1541. The former find for cobalt *1490*, and, from the measurements of several observers, iron would have a melting point of about 1520 on the same scale. These metals are readily oxidized and usually contain sufficient impurities to influence their melting temperatures somewhat. They are most readily worked in an atmosphere of hydrogen. Microscopic samples melted on platinum in hydrogen, as measured by Burgess with an optical pyrometer (see p. 343), gave Ni = 1435, Co = 1464, and Fe = 1505.

Metals Melting above 2000° C. — Above the platinum point, there have been recently a considerable number of attempts to locate fixed points. With the exception of iridium and rhodium, which have already been mentioned, it appears to be necessary to work in vacuo all the elements available in this very high temperature region. A very convenient way to mount them is as filaments or strips as in incandescent lamps.

Of the elements that have been so studied, only tantalum and tungsten have been determined with a fair agreement by several observers; and tungsten is the only one which melts without excessive evaporation, and, having the highest melting point yet measured, appears to be the best adapted for an extreme fixed point.

For *tungsten* the following values have been found:

Waidner and Burgess (1906–1910) ($c_2 = 14,500$)	3250–3050° C.
V. Wartenberg (1907–1910) ($c_2 = 14,600$)	2800–2900
Pirani (1910) ($c_2 = 14,500$)	3250

The value 3000° C. is probably correct to 100° C.

For *tantalum* we have:

V. Bolton (1905)	2250–2300°
Waidner and Burgess (1907 and 1910)	2910
Pirani (1910)	3000
Pirani and Mayer (1911)	2850

Measurements of the melting points of osmium, molybdenum, titanium, and other very refractory elements have also been made, but none of them gives promise of being as serviceable as the above for fixed points in pyrometry.

Melting Points of the Chemical Elements. — In Table II of the Appendix is given a list of the melting points for the chemical elements with some indication of our knowledge of their exactness.

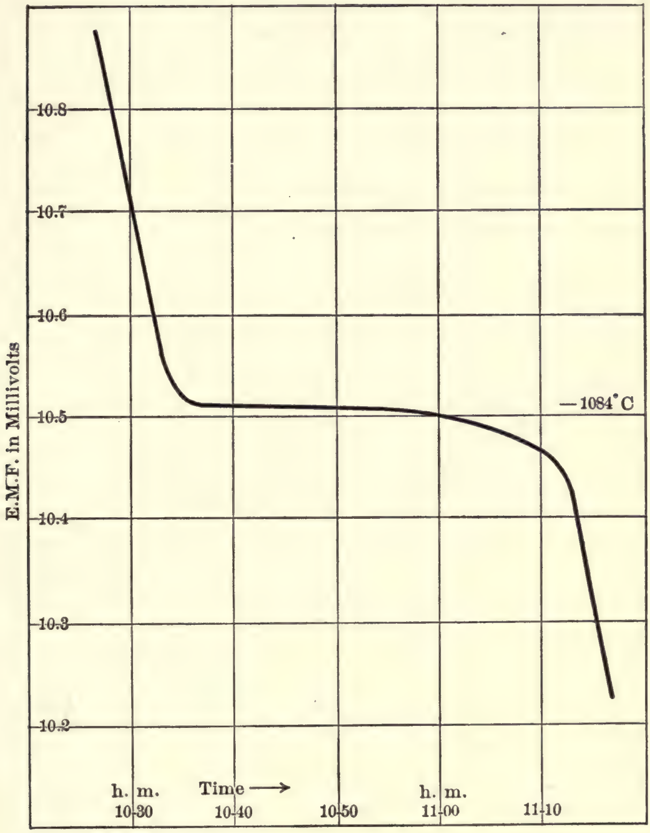

Fig. 170. Freezing of Copper.

Typical Freezing-point Curves. — The freezing-point curves of copper, antimony, silver, and aluminium are shown in Figs. 170 to 173, from data obtained at the Bureau of Standards, in which time in minutes is plotted as abscissa and E.M.F. of a 90 Pt-10 Rh

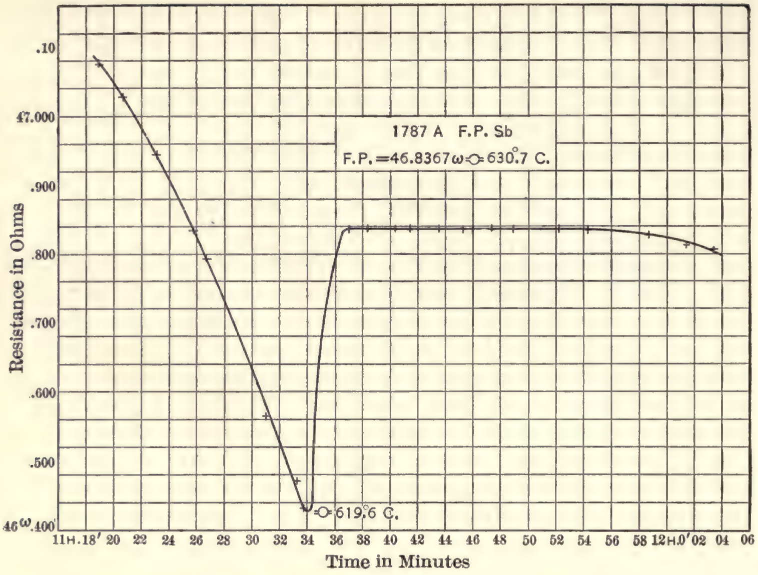

Fig. 171. Freezing of Antimony.

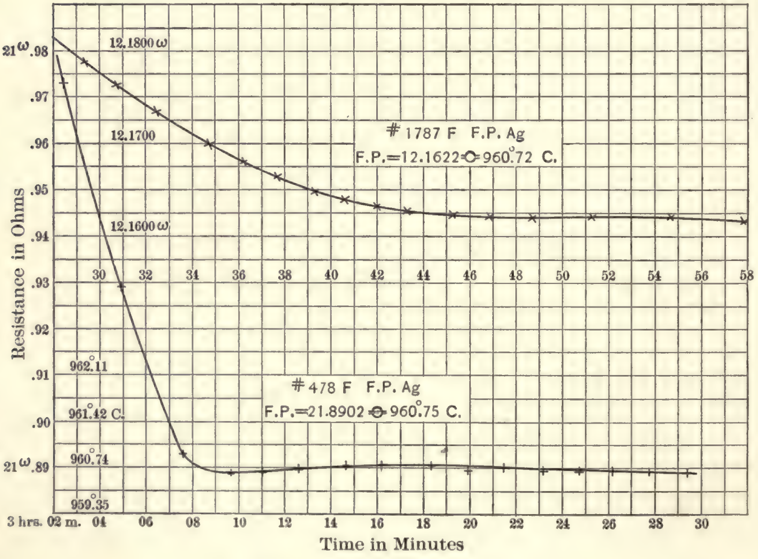

Fig. 172. Freezing of Silver.

thermocouple as ordinate for copper and aluminium, and the resistances of a platinum thermometer for antimony and silver. An inspection of the copper curve shows why this metal is desirable to use, as it gives a very flat curve. With aluminium rapid cooling would be fatal to an exact determination. The slant here observed in the curve at the transition point is characteristic of the presence of impurities and of low conductivity and latent heat. For this metal the melting curve is also given, showing the melting and freezing points to differ somewhat, apparently.

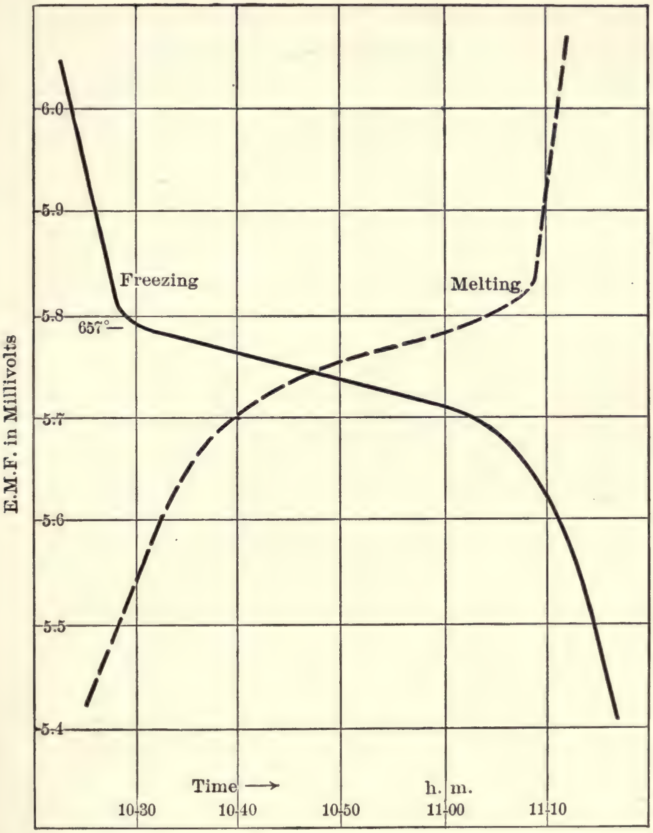

Fig. 173. Freezing and Melting of Aluminium.

Antimony undergoes great undercooling, depending on the rate of cooling, and may reach over 30° C.; but the maximum is a very definite temperature for moderate undercooling, and for a quick-acting thermometer in a charge of metal that is not too small. For silver, two rates of cooling are shown.

Boiling Points. — Sometimes it is desired to calibrate a pyrometer down to room temperature, even if in this case the use of a mercury thermometer is usually to be preferred. Use may be made of the boiling points of water, aniline or naphthaline, and benzophenone, or of the tin freezing point, 231.9°.

Water. — 100° by definition, with a variation of 0.04° for a change of 1 mm. in atmospheric pressure.

Aniline. — 184.1°, with a change of 0.05° per millimeter. This value is probably correct to 0.1°. Aniline, however, oxidizes readily.

Naphthalene. — 218.0°, with a change of 0.058° per millimeter. This point has been very carefully determined by several observers (see page 226), and naphthalene is cheap and readily obtained of sufficient purity, best tested by taking its freezing point, which should be 80.0° C.

Benzophenone.—306.0°, with a change of 0.063° per millimeter. Although expensive and difficult to get pure (melting point = 47.2°), this substance appears to be the only satisfactory one so far found possessing a sufficiently constant boiling point between 218° and 445°. The sulphur boiling-point apparatus (Fig. 169) may be used for both naphthalene and benzophenone if provided with an auxiliary condensing tube. Both these boiling points are easily kept constant to better than 0.05°.

Metallic Salts. — The different fixed points that have been mentioned are not all of a very convenient use. It would be preferable to have in the place of the metals, metallic salts for the determination of the fixed points if they can be shown to be satisfactory otherwise. These salts fortunately are for the most part without action on platinum, which is of great advantage for the standardization of thermocouples and resistance thermometers. There are few, however, whose fusing points have been determined up to the present time in a sufficiently precise manner.

Among the salts whose freezing or melting temperatures have been carefully determined, and which may therefore be used for calibration purposes, are:

NaCl (melting) by W. P. White	801° C.
NaCl (freezing) by G. K. Burgess	800
Na_2SO_4 (melting) by W. P. White	885
Diopside ($CaMg(SiO_3)_2$) (melting) by Day and Sosman	1391
Anorthite ($CaAl_2Si_2O_8$) (melting) by Day and Sosman	1549
Lithium metasilicate (Li_2SiO_3) (melting), F. M. Jaeger	1202
Sodium metasilicate (Na_2SiO_3) (melting), F. M. Jaeger	1088

The transformation points of some salts can only be obtained satisfactorily on heating due to great undercooling when it is attempted to take their freezing points. This is true, for instance, of diopside, anorthite, and the silicates, the values for which apply only for chemically pure salts prepared artificially. Where stirring is practicable the undercooling can largely be avoided in taking freezing points of both metals and salts.

In general, salts give a less sharp melting point than metals, due mainly to low conductivity and heat of fusion of the former, and of course impurities will act in the same way. There is no difficulty, however, in keeping the melting-point curve flat to within 1° C. for some pure salts such as NaCl and N_2SO_4. There are undoubtedly other salts which might be studied to advantage, such as:

	Melting point.
1 MolNaCl + 1 MolKCl	about 650°
Pb_2O_5 2 Na_2O	about 1000
$MgSO_4$	about 1150

K_2SO_4 has been used to some extent, but it appears to possess several dimorphous varieties with different melting points, like sulphur, so that the actual point observed may be uncertain. On page 367 is given a list of salts and the status of their melting points as determined by relatively less precise methods than the above.

Alloys: Eutectic Points. — In the case of certain alloys there are well-defined transition points which may be used as fixed temperatures to advantage in those temperature intervals in which there is no conveniently located and suitable metal freezing point. The most sharply defined of such transformations are the temperatures of freezing of eutectics, when, if the components are pure and the alloy is of very nearly the eutectic composition, the evolution of heat and the constancy of temperature during the transformation compare favorably, in some cases, with the freezing of a pure metal.

Such a suitable eutectic in a desirable location is that of silver and copper, which happens to have the composition Ag_3-Cu_2, whose freezing temperature has been found by Heycock and Neville to be 779.0°, and by Waidner and Burgess 779.2°. There are probably a considerable number of such transformation temperatures that could be used as fixed points to advantage. Thus the eutectics of aluminium or of antimony with the members of the iron group are probably more sharply defined temperatures than those of the commercial metals often used in standardizing thermocouples. Another well-known and fairly reproducible transformation temperature on cooling in the solid state is the recalescent point of steel (iron-carbon), of maximum effect for $C = 0.9\%$ at about 705° C. for slow cooling and somewhat lower for fast cooling.

Reproducibility of Freezing Points. — It is of great importance in pyrometry of precision and in the calibration of instruments to be able to reproduce exactly the fixed temperatures of boiling and freezing or fusion. We have seen that the materials ordinarily used for boiling points can easily be had in sufficient purity to reproduce these temperatures to within 0.05°, and that their freezing points are a delicate test of purity.

There have been several intercomparisons of the thermal reproducibility of some of the metals whose freezing temperatures are used as fixed points. Thus, Day and Allen in 1904, using thermocouples, found that the metals used in the establishment of the Reichsanstalt scale could be purchased in America, with the exception of antimony, to give the same scale to within 1° C. Waidner and Burgess, using both thermocouples and platinum-resistance pyrometers, the latter of which is capable of the much greater sensitiveness and reliability, have made recently an exhaustive study of the reproducibility of several of the metal freezing points, as shown in the following table, in which the samples were purchased from reliable American and German firms as their best product:

Metal	Sn	Cd	Pb	Zn	Sb	Al	Cu
Number of samples............	5	3	4	3	6	3	4
Reproducibility [*] in degrees C.	0.06	.26	.10	.06	2.3	1.2	1.0

There was one or more carefully analyzed sample of each metal, and this table shows that, with the exception of Sb and Al, it is very easy to get these metals pure enough from several sources. The only sufficiently pure antimony was "Kahlbaum," and the best aluminium was from the Aluminium Company of America. The uncertainty noted in the copper point is due mainly to oxidation and the uncertainties of measurement. Of the other metals often used, but not cited in the above table, silver and gold are readily obtained of the highest purity; palladium and platinum less readily so, but their purity as wires is easily tested by measuring their temperature coefficients (see Chapter V).

Temperature of the Arc and Sun. — In certain problems involving extremely high temperatures and as comparison sources for apparent stellar temperatures, the positive crater of the carbon arc and the sun's disk may be used, although the actual values to assign to their temperatures are still somewhat in doubt. In the case of measurements in terms of the radiation laws, it is to be remembered that, other things being equal and barring luminescence, the values found will be low, due to the selective radiation of carbon and of the sun's disk, or the departure of their radiation from the laws of the black body. We should expect, also, that measurements made by total-radiation methods would give lower temperatures than by spectral-radiation methods if the arc and sun have energy distributions differing from those of the black body at the same temperatures.

[*] The reproducibility is defined as the average deviation of the freezing points of the metals from their mean freezing point.

The following measurements have been made on the positive crater of the arc:

TEMPERATURE OF THE CARBON ARC.

Observers.	Date.	Temperature centigrade.	Method.	
Le Chatelier	1892	4100°	Photometric; intensity of red light.	
Violle	1895	3600	Calorimetric; specific heat of carbon.	
Wilson and Gray	1895	3330	Total radiation of copper oxide, empirical relation for.	
Petavel	1898	3830	Total light from Pt; empirical formula.	
Wanner	1900	3430–3630	(Varying with carbons used) photometric in terms of Wien's law, page 251.	
Very	1899	3330–3730	Wien's displacement law.	
Lummer and Pringsheim	1899	3480–3930	Wien's displacement law.	
Féry	1902	3490	Total radiation; Stefan-Boltzman law.	
Féry	1904	3880	Photometric; Wien's law.	
		3343	Total radiation.	
Waidner and Burgess	1904	3420	Holborn-Kurlbaum pyrometer (red and green light).	Wien's law.
		3410	Wanner pyrometer.	
		3450	Le Chatelier optical pyrometer.	

It seems probable that the temperature of the arc is not over 3600° C., and the value 3500° C. appears to best represent the results. Considerable changes in current produce less effect on the apparent temperature than do variations in the kind of carbons used. In taking observation in the arc, it is convenient to mount the positive terminal horizontally and the negative vertically. Care should be taken to have a sufficient area at the maximum temperature, especially when using total-radiation methods. This can only be accomplished by using heavy carbons, 1.5 cm. or more in diameter, and correspondingly high currents.

Observations in terms of several of the radiation laws have been made on the apparent temperature of the sun's disk. Observation shows also that the apparent temperature falls off from the center to the limb, due to absorption in the outer layers, from which it is deduced that the photosphere has a temperature some 500° hotter than the observed value for the center of the disk.

(A) If Stefan's law is assumed to hold, and if the solar constant J as well as the coefficient σ are known, the formula $J=\sigma T^4$, with a proper choice of units, gives us T (absolute) directly; or a calibrated total-radiation pyrometer may be used if the absorption of the earth's atmosphere is corrected for.

(B) If the position of the wave length of maximum energy is known and if the spectral-energy curve for the sun resembles that of the black body, Wien's displacement law $\lambda_m T = C$ may be used if C is known.

(C) Similarly, the relation $E_m T^{-5} =$ const. may also be used.

(D) Finally, Planck's equation, $I = C_1 \lambda^{-5} \left(\epsilon^{\frac{C_2}{\lambda T}} - 1 \right)^{-1}$, gives us still another method if c_2 is known.

If these methods, including measurements with several wave lengths by (D), all gave the same temperature for the sun, using the constants characteristic of the black body in the several equations, it would follow that the apparent temperature found would be the true temperature of the sun. The spectral methods in general, however, appear to give relatively high values, indicating that the true temperature of the sun, except for luminescent effects, is higher than any of the observed values.

Some of the recent observations are given below for the apparent mean value of the temperature of the sun's disk.

SOME RECENT ESTIMATES OF THE SUN'S APPARENT TEMPERATURE.

Observers.	Mean temperature centigrade.	Method.
Millochau and Féry..........	5090–5390	(A) With actinometer (solar constant $=2.8$ to 2.55) and total-radiation pyrometer.
Scheiner........	5930	(A)
Wilsing and Scheiner.....	5130–5600	(D) Using 5 wave lengths, $c_2 = 14{,}600$.
Nordmann.....	5050–5630	Modification of (D) with heterochrome photometer, assumes arc $= 3343°$ C., $c_2 = 14{,}600$.
Abbot and Fowle	6160	(B) $\lambda_m = 0.433\,\mu$; $C = 2930$.
Abbot and Fowle	5570	(A) Solar constant $= 1.95$; Kurlbaum's value of σ (page 247).
Kurlbaum......	5460 or 6120	(D) Using several wave lengths and for c_2, 14,580 or 14,200.

Goldhammer has shown that (B) is probably the least reliable method, and (D) the one least subject to objection if several wave lengths are used. For measurements corrected for the earth's atmosphere, the value 6000° C. would seem to be a fair one for comparison with other celestial sources.

Table of Fixed Points. — In the actual state of our knowledge, the fixed points to which we should give preference are summarized in the table below, in which temperatures below 1600° C. are expressed in terms of the scale of the nitrogen constant-volume thermometer, which has given fairly consistent results to 1100° C., as we have seen, in the hands of several experimenters. Between 1100° and 1600° C. the results of Day and Sosman are followed, and above 1600° temperatures are expressed in terms of Wien's law (page 251), in which c_2 is taken as 14,500, as best representing the data at hand. Estimates of the accuracy with which these fixed points are known, and also of their reproducibility from a known source of supply, are given in the table. The uncertainty of some measuring device is of course included under reproducibility.

TABLE OF FIXED POINTS.

	Boiling points.	Accuracy.	Reproducibility.
Water	100.0° C.	(By definition.)	0.001°
Naphthalene	218.0	0.2	.02
Benzophenone	306.0	0.3	.03
Sulphur	444.7	0.5	.03
	Freezing points.		
Tin	231.9	0.2	0.03
Cadmium	321	0.3	0.05
Lead	327	0.3	0.05
Zinc	419	0.5	0.05
Antimony	631	1.5	0.3
Sodium chloride	800	2.0	1.0
Silver	961	2.0	0.3
Gold	1063	3.0	0.5
Copper	1083	3	1
Lithium metasilicate	1202	5	2
Diopside	1391	10	5
Nickel	1450	15	10
Palladium	1550	15	5
Platinum	1755	20	10
Tungsten	3000	100	25
Carbon arc	3500	150	50
Sun	6000	500	100

Standardization of Pyrometers. — The above discussion has shown that we possess a number of fixed points which have been established with sufficient accuracy to use them in the standardization of pyrometers. For such standardization, two courses are open besides direct comparison with a gas thermometer, a proceeding usually out of the question, and furthermore rendered superfluous by the establishment of these fixed points in terms of the gas scale. When its construction permits, a pyrometer may be calibrated by finding its indications at two or more of the fixed points, or may be compared with another which has been so calibrated. The latter method is the one used for ordinary purposes, as in the graduation of industrial instruments, but for pyrometers which are to be used as standards the former method should be used when possible.

We have discussed at some length, in their respective chapters, the methods of calibration for the various pyrometers, and it is unnecessary to dwell further on this matter, except to say that it cannot be assumed that a pyrometer once standardized is standardized for all time, especially if it is subjected to hard usage.

Standardizing Laboratories. — Recognizing the importance of establishing, preserving, and disseminating a common and authoritative temperature scale and of providing means of having pyrometers and other instruments certified as to their accuracy, some of the governments have established laboratories, such as the Physikalisch-Technische Reichsanstalt in Germany, the National Physical Laboratory in England, the National Bureau of Standards in the United States, and the Laboratoire d'Essais and the Laboratoire Central d'Electricité in France, whose functions are not only testing instruments but carrying on researches as well. The German institution, the oldest of these laboratories, has been one of the most potent factors in the development of excellency in German instruments, and has been of immense service to the industries as well as to the interests of science; and the other national laboratories are fast assuming a position of equal importance in their respective countries.

Metals and Salts of Certified Melting Points. — It would often be of great convenience, when one has to calibrate his own pyrometer, and in cases of dispute between individuals as to their respective temperature scales, to have available metals or salts the melting points of which had been certified by a standardizing laboratory. The Bureau of Standards is preparing to issue such certified metals and salts of sufficient range and number to meet the ordinary requirements of pyrometer calibration.

Electrically Heated Furnaces. — For the standardization of pyrometers as well as in many other high-temperature problems, it is necessary to preserve a constant temperature for a considerable time and to be able to reproduce a given temperature very exactly.

Electrically heated resistance furnaces best serve these ends, and great improvements have been made in their construction in recent years.

Furnaces wound with nickel wire of 1 to 2 mm. diameter on porcelain have been used considerably, but they are slow in heating up and their upper limit is about 1200° C., if the furnace is to be used frequently, although for a single heating 1400° C. may be attained with care. Platinum wire has been used to attain higher temperatures, but the use of this material in wire form is very expensive for heating.

Heræus has made electric heating to 1300° or 1450° C., depending on size of furnace, generally accessible by the substitution of platinum foil for the wire, weighing about 1.5 grams per square centimeter or having a thickness of about 0.007 mm. This reduces the cost of a platinum furnace very greatly, and has the further advantages of giving slightly greater uniformity of heating and attaining at a somewhat greater speed high temperatures than with wire-wound furnaces. Above 1500° C. chemical action sets in between the platinum and material of the tubes usually employed, so that although, as far as the platinum is concerned, 1700° C. could be maintained for a short time, yet the present safe upper limit for long periods of heating is 1400° with foil furnaces.

Their greatest weakness is the cracking of the porcelain tubes on which the foil is wound and the evaporation of the platinum when not covered with a suitable paste.

For very high temperatures, up to 2100°, the iridium-tube furnaces of Heræus may be used, as they have been with success by Nernst and others in the study of vapor pressures at these temperatures, as well as in melting point and physiochemical investigations. In Fig. 174 is shown the furnace and accessories used by Waidner and Burgess for the determination of the palladium and platinum melting points. For lower temperatures, tubes of platinum or of a platinum alloy may be used with great saving in cost.

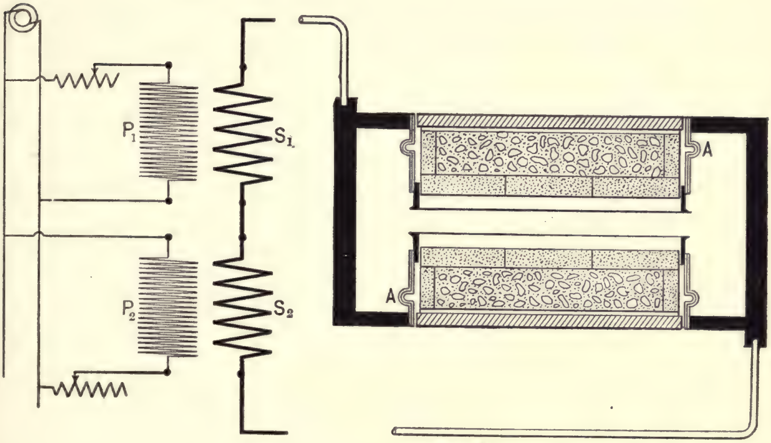

Fig. 174. Iridium-tube Furnace.

Crucible Furnaces. — A suitable form of electrically heated crucible furnace for freezing and melting point determinations to 1100° C., such as used at the Bureau of Standards, is shown in Fig. 175. The double winding with platinum ribbon gives a very delicate temperature control if connected in parallel through separate rheostats on the same battery. This furnace is designed to carry a crucible of 300 c.c. capacity, so as to give ample immersion of the thermometer at a constant temperature. If the freezing or melting of a metal is made to take twenty minutes or more, the form of the freezing or melting curve becomes a very sensitive check on the purity of the sample. Another form of crucible furnace used successfully at the Carnegie Geophysical Laboratory to above 1600° C. is shown in Fig. 52. The characteristic of this furnace is the inwound platinum-wire heating

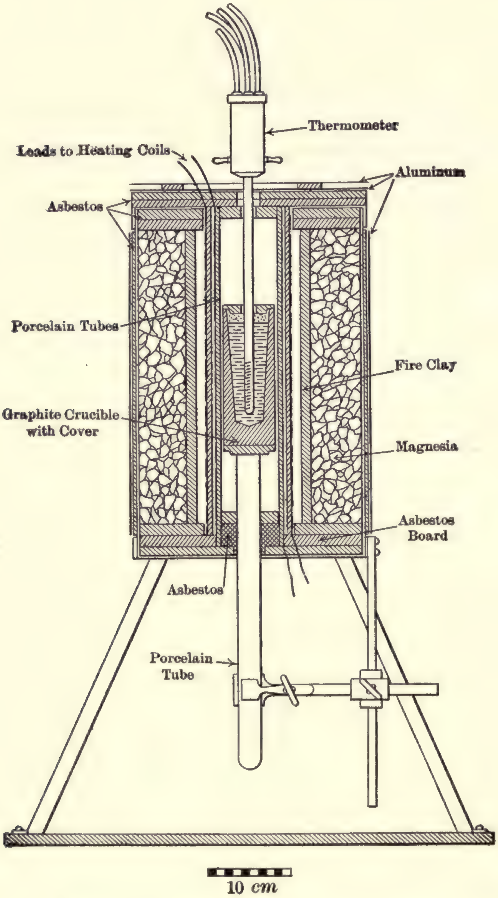

Fig. 175. Double-wound Crucible Furnace.

coil. Although of high first cost, it is a very durable furnace as constructed. Both types of furnace may be arranged for use with any desired atmosphere. Less satisfactory results will be obtained with ordinary gas furnaces to 1300° C.

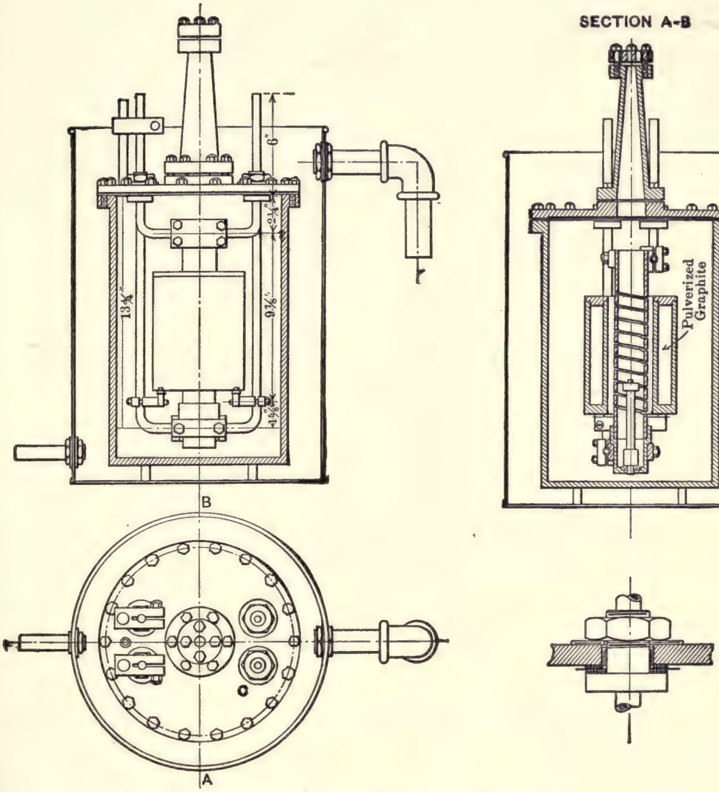

Fig. 176. Arsem Vacuum Electric Furnace.

Vacuum and Pressure Furnaces. — Mr. Arsem of the General Electric Company has developed a type of vacuum furnace which is convenient for certain melting points, such as fireclays, refractory bricks, and ashes, and chemical investigations to 2500° C. or higher. In one of its ordinary water-cooled forms, shown in Fig. 176, the heating is produced by passing an alternating current of low voltage through a graphite spiral. The highest temperatures may be reached in a few minutes. The interior is observed through a mica or glass window. Temperatures are measured with an optical pyrometer. By taking the heating curve, the transformation points for only a few tenths grams of material are easily observed. (See page 342.) Such a furnace has been in constant use at the Bureau of Standards for several years.

V. Wartenberg has successfully constructed a tube resistance furnace of tungsten mounted in vacuo (Fig. 177), and with it determined the melting points of a number of refractory elements melting above 2000° C.

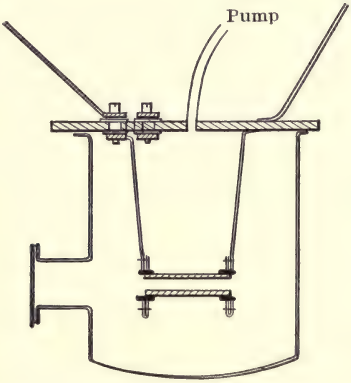

Fig. 177. Wartenberg's Tungsten Furnace.

Messrs. Hutton and Petavel of Manchester, England, have constructed a pressure furnace for work at high temperatures, the essential parts of which are shown in Fig. 178. A vertical carbon tube was electro-coppered at the ends, soldered into brass castings, and provided with water circulation at *A* and *B*. Temperature readings were taken down the side tube of carbon, fixed into a brass tube with a window at the end, a current of hydrogen being admitted at *C*. The whole furnace was packed in crushed wood charcoal, while a thin walled graphite crucible contained the metal to be studied. This furnace has been used by Greenwood for the determination of the boiling points of some of the metals and their variation with pressure. Other types of furnace are described in Chapters II, IV, and V.

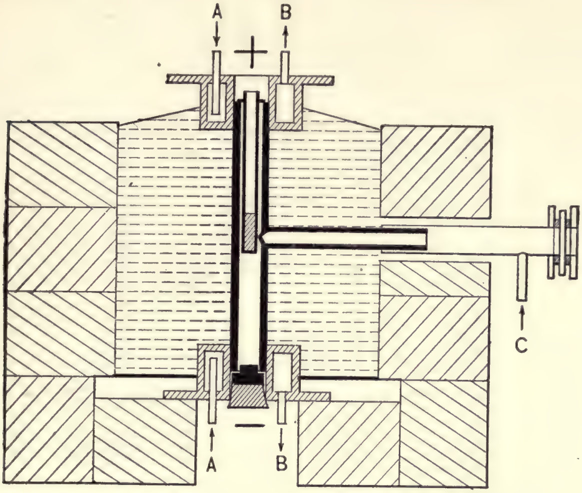

Fig. 178. Graphite Furnace of Hutton and Petavel.

BIBLIOGRAPHY.

GENERAL WORKS.

(The heavy figures refer to volumes.)

Weinhold. — Principles of construction of pyrometers. Pogg. Ann., **149,** p. 186; 1873.

C. H. Bolz. — Die Pyrometer, Eine Kritik der bisher construirten höher Temperaturmesser in wissenschaftlich-technische Hinsicht, 1888.

C. Barus. — Die physikalische Behandlung und die Messung höher Temperaturen, 1892, Leipzig. — Bull. U. S. Geological Survey No. **54,** 1889; No. **103,** 1893.

Kayser. — Handbuch der Spectroscopie, Bd. **2,** 1902. Summary of radiation methods.

Callendar. — Measurement of Extreme Temperatures. Nature, **59,** 1899.

C. W. Waidner. — Methods of Pyrometry. Proc. Eng. Soc. Western Pennsylvania, Sept., 1904.

Waidner and Burgess. — Establishment of High-temperature Scale. Phys. Rev., **24,** p. 441; 1907.

Burgess. — Estimation of High Temperatures. Proc. Am. Electroch. Soc., **11,** p. 247; 1907.

Chwolson. — Traité de Physique. (Instruments, Theory, Bibliography.)

Leber. — Ch. XIV in *Geiger's* Handbuch der Eisen- und Stahlgiesserei, 1911.

NORMAL SCALE OF TEMPERATURES.

Carnot. — Reflections on the motive power of fire.

Lippmann. — Thermodynamics, p. 51.

Thomson and Joule. — Philosophical Transactions of the Royal Society, **42,** p. 579; 1862.

Thomson (*Lord Kelvin*). — Collected Papers, **1,** p. 174.

Lehrfeldt. — Philosophical Magazine, **45,** p. 363; 1898.

Callendar. — Phil. Trans., **178,** pp. 161–220; 1888.

Regnault. — Account of his investigations, **1,** p. 168; 1847.

Chappuis. — Studies of the gas thermometer. Trav. du Bureau International des Poids et Mesures, **6,** 1888.

Chappuis and Harker. — Trav. et Mém. du Bureau Int. des Poids et Mesures, 1900. Phil. Trans., 1900.

Schreber. — Absolute Temperature. W. Beibl., **22,** p. 297; 1898.

D. Berthelot. — Reduction of gas-thermometer readings to the absolute scale. Trav. et Mém. du Bureau Int., **13,** 1903. C. R., **138,** p. 1153; 1904.

Boltzmann. — On the determination of absolute temperature. Wied. Ann., **53,** p. 948; 1894.

E. Mach. — Theory of Heat.

Callendar. — Thermodynamical correction to gas thermometer. Phil. Mag., May, 1903.

Rose-Innes. — Phil. Mag. (6), **2,** p. 130; 1901.

Pellat. — C. R., **136,** p. 809; 1903.

Chappuis. — Jl. de Phys., **3,** p. 833; 1904. Ann. des Poids et Mesures, **13,** p. a3; 1907.

Berthelot. — Ann. des Poids et Mesures, **13,** p. b3; 1907.

Buckingham. — Bull. Bureau Standards, **3,** p. 237; 1907.

Rose-Innes. — Phil. Mag., **14,** p. 301; 1908.

GAS PYROMETER.

Prinsep. — Ann. Chim. et Phys., 2d Series, **41,** p. 247; 1829.

Pouillet. — Treatise on Physics, 9th ed., **1,** p. 233; 1858. Comptes Rendus, **3,** p. 782; 1836.

Ed. Becquerel. — C. R., **57,** pp. 855, 902, 955; 1863.

Sainte-Claire-Deville and Troost. — C. R., **90,** pp. 727, 773; 1880. **45,** p. 821; 1857. **49,** p. 239; 1859. **56,** p. 977; **57,** pp. 894, 935; 1863. **98,** p. 1427; 1884. **69,** p. 162; 1864. Ann. Chim. et Phys. (3), **58,** p. 257; 1860. Répert. Chim. Appl., p. 326; 1863.

Violle. — Specific heat of platinum. C. R., **85,** p. 543; 1877. Specific heat of palladium. C. R., **87,** p. 98; 1878. **89,** p. 702; 1879. — Boiling point of zinc. C. R., **94,** p. 721; 1882.

V. and C. Meyer. — Density of halogens. Ber. D. Ch. Ges., **12,** p. 1426; 1879.

Barus.—Bull. U. S. Geological Survey No. **54,** 1889. Phil. Mag. (5), **34,** p. 1; 1892. — Report on Pyrometry, Congress at Paris, 1900.

Regnault.—Account of his experiments, **1,** p. 168; Paris, 1847. Mém. de l'Institut, **21,** pp. 91, 110; 1847. Ann. Chim. et Phys. (3), **68,** p. 89; 1861.

Holborn and Wien. — Bull. de la Soc. pour l'encouragement (5), **1,** p. 1012; 1896. Wied. Ann., **47,** p. 107; 1892. **56,** p. 360; 1895. Zeits. für Instrum, p. 257; 1892.

Crafts and Meier. — Vapor density of iodine. C. R., **90,** p. 690; 1880.

Langer and V. Meyer. — Pyrochemical Researches (Brunswick), 1885.

Joly. — Pogg. Ann., Jubelband, p. 97; 1874.

Randall. — Permeability of platinum. Bull. Soc. Chim., **21,** p. 682; 1898.

Mallard and Le Chatelier. — Ann. des Mines, **4,** p. 276; 1884.

J. R. Erskine Murray. — On a new form of constant-volume air thermometer. Edinburgh Proc., **21,** p. 299; 1896–97. Journ. Phys. Chem., **1,** p. 714; 1897.

J. Rose-Innes. — The thermodynamic correction for an air thermometer, etc. Nature, **58,** p. 77; 1898. Phil. Mag. (5), **45,** p. 227; 1898. **50,** p. 251; 1900. Proc. Phys. Soc. London (1), **16,** p. 26; 1898.

Chappuis. — Phil. Mag. (5), **50,** p. 433; 1900. (6), **3,** p. 243; 1902. Report for Paris Congress, 1900; Jour. de Phys., Jan., 1901, p. 20.

D. Berthelot. — On a new method of temperature measurement. C. R., **120,** p. 831; 1895. Ann. Chim. et Phys. (7), **26,** p. 58; 1902.

Holborn and Day.—Wied. Ann., **68,** p. 817; 1899. Am. Jour. Sci. (4), **8,** p. 165; 1899. Zeitscher. Instrum., May, 1900. Am. Jour. Sci. (4), **10,** p. 171; 1900. Drude's Ann., **2,** p. 505; 1900.

Chappuis and Harker. — Trav. et Mém. du Bureau Int. des Poids, 1900, 1902. — Phil. Trans., 1900.

Callendar. — Phil. Mag., **48,** p. 519; 1899. Proc. Roy. Soc., **50,** p. 247; 1891.

Callendar and Griffiths. — Phil. Trans., **182,** 1891.

D. Berthelot. — On gas thermometers and the reduction of their indications to the absolute scale. Trav. et Mém. du Bureau Int., **13,** 1903.

Travers. — Studies in Gases (Macmillan). — Proc. Roy. Soc., **70,** p. 485.

Kapp. — Ann. der Phys., **5,** p. 905; 1901.

Wiebe and Böttcher. — Gas thermometry, Berich. Berlin Akad., **44,** p. 1025. Inst'kunde, 1888.

Jaquerod and Perrot. — Various gases in quartz. C. R., **138,** p. 1032; 1904.

Day and Clement. — Am. Jl. Sci., **26,** p. 405; 1908.

Day and Sosman. — Scale 400° to 1550° C. Am. Jour. Sci. (4), **29,** p. 93; 1910. Pub. 157, Carnegie Institution of Washington, 1911.

A. L. Day. — Met. and Chem. Eng., **8,** p. 257; 1910.

Holborn and Valentiner. — Ann. der Phys. (4), **22,** p. 1; 1907.

Berthelot. — Value of gas constant. Zs. Elektroch., **10,** p. 621; 1904.

Jaquerod and Perrot. — Expansion coefficients. C. R., **140,** p. 1542; 1905.

Holborn and Henning. — Ann. der Phys. (4), **35,** p. 761; 1911.

CALORIMETRIC PYROMETER.

(*See also* Specific Heat.)

Violle. — Boiling and fusing points. C. R., **89,** p. 702; 1879.

Le Chatelier. — Sixteenth Congress of the Société technique de l'industrie du gaz, June, 1889.

Euchêne. — Thermal relations in the distillation of oil. (Monograph.)

Ferrini. — Rend. Lomb., **35,** p. 703; 1902.

Berthelot. — Calorimetry. Ann. Chim. et Phys. (4), **20,** p. 109; (5), **5,** p. 5; (5), **10,** pp. 433, 447; (5), **12,** p. 550.

Hoadley. — Trans. Am. Inst. Mech. Engs., **2,** No. 23, p. 42; **3,** No. 65, p. 187.

THERMOELECTRIC PYROMETER.

Becquerel. — Ann. Chim. et Phys. (2), **31,** p. 371; 1826.

Pouillet.—Traité de Physique, 4th ed., **2,** p. 684; C. R., **3,** p. 786; **4,** p. 513; 1836.

Ed. Becquerel. — Annales du Conservatoire, **4,** p. 597; 1864. C. R., **55,** p. 826; 1862. Ann. de Chim. et de Phys. (3), **68,** p. 49; 1863.

Tait. — Thermoelectric power. Trans. Roy. Soc. Edinb., **27,** p. 125; 1872–73.

Regnault. — Account of investigations on heat engines, **1,** p. 240. C. R., **21,** p. 240; 1847. (Fe–Pt couple.)

Knott and MacGregor. — Graphical representations. Trans. Roy. Soc. Edinb., **28,** p. 321; 1876–77.

Seebeck. — Fundamental principles. Pogg. Ann., **6,** pp. 133, 263; 1826.

Cumming. — Inversion points. Trans. Cambridge Soc., **2,** p. 47; 1823.

Draper. — Phil. Mag. (3), **16,** p. 451; 1840.

Mousson. — Arch. d'Elec. (Geneva), **4,** p. 5; 1844. (Inhomogeneity.)

Magnus. — Pogg. Ann., **83,** p. 469; 1851. (Inhomogeneity.)

Thomson. — Trans. Edinb. Soc., **21,** p. 123; 1854. Phil. Mag. (4), **11,** pp. 214, 281, 379, 433; 1856. C. R., **39,** p. 116; 1854. Phil. Trans., **146,** p. 649; 1856.

Avernarius. — Formulæ and various couples. Pogg. Ann., **119,** p. 406; 1863. **122,** p. 193; 1864.

Kleminic and Czermak. — Pt–Cu–Ni–Fe couples. Wied. Ann., **50,** p. 175; 1893.

Le Chatelier. — Thermoelectric pyrometer. C. R., **102,** p. 819; 1886. Journal de Phys. (2), **6,** Jan., 1887; Genie civil, March 5, 1887; 16th Congress of the Société technique de l'industrie du gaz, June, 1889; Bull. de la Société de l'encouragement, 1892; Bull. Soc. Chim. Paris, **47,** p. 42; 1887.

Barus. — Washington, 1889, Bull. of the U. S. Geological Survey, No. **54,** and No. **103** (No. **54** contains a very complete historical account of the whole subject of pyrometry). Phil. Mag. (5), **34,** pp. 15, 376; 1892. Am. Jour. Sci., **36,** p. 427, 1888; **47** (3), p. 366; **48,** p. 336; 1894. (Pt · Pt–Ir couples; formulæ.)

Holborn and Wien. — Wied. Ann., **47,** p. 107; 1892. **56,** p. 360; 1895. Zeit. des Vereines deutscher Ingenieure, **41,** p. 226; 1896. Stahl und Eisen, **16,** p. 840. (Pt · Pt–Rh couples.)

Roberts-Austen. — Recent progress in pyrometry. Trans. Am. Institute of Mining Engineers, 1893. (*See also* Recording Pyrometers.)

E. Damour. — Bull. de l'Assoc. amicale des anciens élèves de l'Ecole des Mines, March, 1889.

H. Howe. — Pyrometric data. Engineering and Mining Journal, **50,** p. 426; 1890. Metallurgical laboratory notes (expts. with thermocouples), 1902.

Holborn and Day. — Pt alloys. Ann. d. Phys. (4), **2,** p. 505; 1900. On the melting point of gold. Ann. d. Phys. (**4**), p. 99; 1901. Am. Jour. Sci., **11,** p. 145; 1901. — On the thermoelectric properties of certain metals. Sitz. Berl. Akad., p. 69; 1899. Am. Jour. Sci. (4), (**8**), p. 303; 1899. Mitth. Phys.-tech. Reichsanst., **37,** 1899.

Stansfield. — Pt alloys, formulæ. Phil. Mag. (5), **46,** p. 59; 1898.

Holman. — Exponential formulæ. Phil. Mag., **41,** p. 465; 1896. Proc. Am. Acad., **31,** p. 234.

Holman, Lawrence, and Barr. — Phil. Mag., **42,** p. 37; 1896. Proc. Am. Acad., **31,** p. 218.

Schoentjes. — Arch. de Phys. (4), **5,** p. 136; 1898.

Noll. — Thermoelectricity of chemically pure metals. Wied. Ann., p. 874; 1894.

Steinmann. — Thermoelectricity of certain alloys. C. R., **130,** p. 1300; **131,** p. 34; 1900.

Belloc. — Thermoelectricity of steels. C. R., **131,** p. 336; 1900. Ann. Chim. et Phys., **30,** p. 42; 1903. C. R., **134,** p. 105; 1902.

D. Berthelot. — On the graduation of couples. C. R., **134,** p. 983; 1902.

Thiede. — Freezing-point apparatus. Zs. Angew. Ch., **15,** p. 780; 1902.

Lindeck and Rothe. — The standardization of thermoelements for high-temperature measurements (as carried out at the Phys. Tech. Reichsanstalt). Zs. Instrument'k., **20,** p. 285; 1900, and following years.

Nichols. — Temperature of flames, etc., with thermocouple. Phys. Rev., **10,** p. 234; 1900.

Harker. — Gas *vs.* thermoelectric scales. Phil. Trans., **203,** p. 343; 1904.

Chauvin and Arnoux. —Compound couple. Bull. Soc. d'Encourag., **109,** p. 1171; 1907.

Crompton. — Fe–Ni, Fe–Cu. Lond. Electrician, **56,** p. 808; 1906.

Bristol. — Pyrometers. Am. Soc. Mech. Eng., **27,** p. 552; 1906. Am. Machinist, p. 201; 1906. Electrochem. and Met. Ind., **4,** p. 115; 1906.

Pécheux. — Le pyromètre thermoeléctrique, Paris, 1909. (Ni–Cu, etc., couples.) C. R., **139,** p. 1202; 1904. **148,** p. 1041; 1909. **149,** p. 1062; 1909.

Broniewski. — Thermoelectric properties of alloys (with a bibliography, 1822–1909). Rev. de Métallurgie, **7,** p. 45; 1910.

C. H. Wilson. — Electrochem. and Met. Ind., **7,** p. 116; 1909.

Barrett. — Phil. Mag. (5), **49,** p. 309; 1900. (Fe–Ni–Mn to 1000° C.)

Harrison. — Fe–Ni–Cu alloys to 1050° C. Phil. Mag. (6), **3,** p. 177; 1902.

Boudouard. — Steels 0–1200° C. Rev. d. Métallurgie, **1,** p. 80; 1904.

Hevesy and Wolff. — Ni–Ag couple. Phys. Zs., **11,** p. 473; 1910.

Stupakoff. —Pamphlets on Industrial Practice.

Schneider. — Thermoelectric powers of heated wires. Elektrotech. Zs., **25,** p. 233; 1904.

Hirschson. — C–Ni couple. Zs. Chem. Apparatk., p. 622; 1907.

Sosman. — Pt–Rh. Am. Jour. Sci., **30,** p. 1; 1910.

Day and Allen. — Pt–Rh to 1600° C. Phys. Rev., **19,** p. 177; 1904.

Palmer. — Fe–Cu 0–200°. Phys. Rev., **21,** p. 65; 1905.

A. Campbell. — Composite thermocouples. Phil. Mag., **9,** p. 713; 1905.

White. — Constancy of thermoelements. Phys. Rev., **23,** p. 449; 1906. Melting-point methods. Am. Jour. Sci., **28,** p. 453; 1909.

Geibel. — The noble metals. Zs. Anorg. Ch., **69,** p. 38; 1910. **70,** p. 240; 1911.

Waidner and Burgess. — Comparison of thermoelectric and resistance scales. Bull. Bur. Standards, **6,** p. 182; 1910.

Memmler and Schob. — Mitt. K. Material prüfungsamt, **28,** p. 307; 1910. (Use in testing machine.)

CORRECTIONS FOR COLD JUNCTIONS.

C. Offerhaus and E. H. Fischer. — Electrochem. and Met. Ind., **6,** p. 362; 1908.

R. Vogel. — Zs. Anorg. Chem., **45,** p. 13; 1905.

Schultze and Koepsel. — Centralb. Accumulatoren, **8,** p. 102; 1907.

POTENTIOMETERS FOR TEMPERATURE MEASUREMENTS.

Fuessner. — Zs. f. Instrumentenkunde, **10,** p. 113; 1890.

Lehrfeldt.— Phil. Mag., **5,** p. 668; 1903.

Varley. — Brit. Assoc., **36,** p. 14; 1866.

Raps. — Zs. f. Instrumentenkunde, **15,** p. 215; 1895. Elektrotech. Zs., **16,** p. 507; 1895. **24,** p. 978; 1903.

Franke. — Elektrotech. Zs., **24,** p. 978. Zs. f. Instrumentenkunde, **24,** p. 93; 1904.

Harker. — Phil. Mag., **6,** p. 41; 1903.

Holman. — Phil. Mag., **42,** p. 37; 1896.

Lindeck. — Zs. f. Instrumentenkunde, **20,** p. 293; 1900.

Hausrath. — Ann. der Phys., **17,** p. 735; 1905. Zs. f. Instrumentenkunde, **27,** p. 309; 1907.

Diesselhorst. — Zs. f. Instrumentenkunde, **26,** pp. 173, 297; 1906. **28,** p. 1; 1908.

White. — Zs. f. Instrumentenkunde, **27,** p. 210; 1907. Phys. Rev., **25,** p. 334; 1907.

Wenner. — Phys. Rev., **31,** p. 94; 1910.

ELECTRICAL RESISTANCE PYROMETER.

Müller. — Pogg. Ann., **103,** p. 176; 1858.

W. Siemens. — Proc. Royal Soc., **19,** p. 351; 1871. Bakerian Lecture, 1871. Transactions of the Society of Telegraph Engineers, 1879. British Association, p. 242; 1874.

Benoït. — C. R., **76,** p. 342; 1873.

Callendar. — Phil. Trans. of R. S., **178,** pp. 160–230; 1888. Proc. Roy. Soc. Lond., **41,** p. 231; 1886. Phil. Trans., 1887. Phil. Trans., p. 119; 1892 (with *Griffiths*). — Platinum pyrometers. Iron and Steel Institute, May, 1892. Phil. Mag., **32,** p. 104; 1891. **33,** p. 220; 1892. — Proposals for a standard scale of temperatures. B. A. Report, 1899; Phil. Mag., **47,** pp. 191, 519; 1899, is a résumé of the question. Phil. Trans., **199,** p. 1; 1902. — Steam temperatures. Br. Assoc. Rept., p. 422; 1897. (Ibid. with *Nicholson*) Proc. Inst. C. E., p. 131; 1898. — Gas-engine Cylinders, with *Dalby.* Engineering (Lond.), **84,** p. 887; 1907.

Heycock and Neville. — Determination of high temperatures. Jour. of Chem. Society, **67,** pp. 160, 1024; 1895. Phil. Trans., **189,** p. 25; 1897. **202,** pp. 1–69.

Barus. — Amer. Jour. Sci. (3), **36,** p. 427; 1888.

Holborn and Wien. — Ann. der Phys., **47,** p. 107; 1892. **56,** p. 360; 1895. Bull. de la Soc. d'encouragement, 5th Series, **1,** p. 1012; 1896.

Chappuis and Harker. — A comparison of platinum and gas thermometers made at the B. Int. des Poids et Mesures. B. A. Report, 1899; Trav. et Mém. du Bureau Int. des Poids et Mesures, 1900, 1902; Phil. Trans., 1900; Jour. de Phys., **10,** p. 20; 1901. Proc. Roy. Soc., **65,** p. 377; 1899.

Appleyard. — Phil. Mag. (5), **41,** p. 62; 1896.

Dickson. — Formulæ Phil. Mag. (5), **44,** p. 445; 1897. **45,** p. 525; 1898.

Wade. — Wied. Beibl., **23,** p. 963; 1899. Proc. Cambr. Soc., **9,** p. 526; 1898.

Waidner and Mallory. — Phys. Rev., **8,** p. 193; 1899.

Barnes and McIntosh. — New form of platinum thermometer. Phil. Mag., **6,** p. 353; 1903.

Tory. — Br. Assoc. Rpt., p. 588; 1897. Phil. Mag., **50,** p. 421; 1900.

Whipple. — Temperature indicator, etc. Phys. Soc. (Lond.), **18,** p. 235; 1902.

Chree. — Platinum Thermometry at the Kew Observatory. Proc. Roy. Soc., **67,** p. 3.

Harker. — On the high-temperature standards of the National Physical Laboratory. Proc. Roy. Soc., **73,** p. 217; 1904.

Jaeger. — Precision of Resistance Methods. Zs. Instr'kunde, **26,** p. 69; 1906.

Burstall. — Rapidly varying temperatures. Phil. Mag., **40,** p. 282; 1895. Proc. Inst. Mech. Engrs., p. 1031; 1901.

Hopkinson. — Gas-engine Temperatures. Engineering, **81,** p. 777; 1906. Phil. Mag., **13,** p. 84; 1907.

H. Edwards. — Contr. Jefferson Lab., **2,** p. 549; 1904. Proc. Am. Acad., **40,** No. 14.

Marvin. — Nickel to 300° C. Phys. Rev., **30,** p. 522; 1910. — Direct-reading Bridge for Ni and Pt. Jour. Frankl. Inst., **171,** p. 439; 1911.

Travers and Gwyer. — Scale 444° to − 190°. Proc. Roy. Soc., **74,** p. 528; 1905.

A. Campbell. — Direct Reading. Phil. Mag., **9,** p. 713; 1905.

Waidner and Burgess. — Pt and Pd to 1100° C. Bull. Bureau Standards, **6,** pp. 149–230; 1909. (Contains bibliography of about 135 titles.)

Holborn and Henning. — Pt *vs.* Gas Therm. to S.B.P. Ann. der Phys. (4), **26,** p. 835; 1908. **35,** p. 761; 1911.

Clark, Fisher, and Wadsworth. — Pyrometer Bridge. Electrician, **60,** p. 376; 1906.

Harris. — Deflectional Bridge Pyrometer. Electrician, **62,** p. 430; 1908.

Cambridge Co. — Callendar and Griffiths Bridge. Electrician, **60,** p. 477; 1906.

Bruger. — Hartmann and Braum Instrument. Elektrotech. Zs., **27,** p. 531; 1906.

E. F. Northrup. — Measurement of Temperature by Electrical Means. Am. Inst. Elec. Eng., **25,** pp. 219, 473; 1906.

LAWS OF RADIATION.

EARLY WORK.

Newton. — Opuscula Mathematica, **2,** p. 417.

Prevost. — Sur l'équilibre du feu, Geneva, 1792, 1809.

Dulong and Petit. — Ann. Chim. et Phys., **7,** pp. 225, 337; 1817.

Kirchhoff. — Pogg. Ann., **109,** p. 275; 1860. Ann. Chim. et Phys., **59,** p. 124; 1860.

B. Stewart. — Edinburgh Trans., 1858; Proc. Roy. Soc., **10,** p. 385; 1860.

Provostaye and Desains. — Ann. Chim. et Phys., 1860–1865.

Draper. — Am. Jour. Sci., **4,** p. 388; 1847.

Becquerel. — C. R., **55,** p. 826; 1862.

Clausius. — Pogg. Ann., **121,** p. 1; 1864.

F. Rosetti. — Phil. Mag. (5), **7,** pp. 324, 438, 537; 1879.

Violle. — C. R., **88,** p. 171; 1879. **92,** pp. 866, 1204; 1881. **105,** p. 163; 1887.

Weber. — Wied. Ann., **32,** p. 256; 1887.

Tait. — Edinb. Proc., **12,** p. 531; 1884.

Tyndall. — Phil. Mag., **28,** p. 329; 1864. — The laws of radiation and absorption. Mém. by Prevost, Stewart, Kirchhoff, and Bunsen, edited by D. B. Brace. Am. Bk. Co., 1902.

Ritchie. — Mutual radiation. Pogg. Ann., **38,** p. 378; 1866.

RECENT WORK.

Kayser. — Handbuch der spectroscopie, **2,** 1902. (Contains an admirable summary of the work on radiation.)

Drude. — Theory of Optics (Engl. trans. pub. by Longmans).

Stefan. — On the relation between heat radiation and temperature. Wien. Ber., **79,** B. 2, p. 391; 1879.

Schleirmacher. — On Stefan's law. Wied. Ann., **26,** p. 287; 1885.

Boltzmann. — Deduction of Stefan's law. Wied. Ann., **22,** p. 291; 1884.

Paschen. — On the emission of heated gases. Wied. Ann., **50,** p. 409; 1893. **51,** p. 1; 1894. **52,** p. 209; 1894. — On the emission of solids. Wied. Ann., **49,** p. 50; 1893. **58,** p. 455; 1896. **60,** p. 662; 1897. Astrophys. Jour., **2,** p. 202; 1895. — On black-body radiation. Wied. Ann., **60,** p. 719; 1897. Berl. Ber., p. 959; 1899. Ann. der Phys., **4,** p. 277; 1901. **6,** p. 646; 1901.

Paschen and Wanner. — On a photometric method, etc. Berl. Ber., p. 5; 1899.

Wanner. — Photometric measurement of black-body radiation. Ann. der Phys., **2,** p. 141; 1900.

Féry. — Radiation from oxides. Ann. Chim. Phys. (7), **27,** p. 433; 1902.

Petavel. — Heat dissipated by platinum, etc. Phil. Trans., **191,** p. 501; 1898. **197,** p. 229; 1901.

Milliken. — Polarization of light from incandescent surfaces. Phys. Rev., **3,** p. 177; 1895.

Langley. — Distribution of energy in solar spectrum, etc. Am. Jour. Sci., **31,** p. 1; 1886. **36,** p. 367; 1888. Phil. Mag. (5), **26,** p. 505; 1888.

Wilson and Gray. — Temperature of arc and sun. Proc. Roy. Soc., **55,** p. 250; 1894. **58,** p. 24; 1895.

W. Michelson. — Theoretical study of the distribution of energy in the spectra of solids. Jour. de Phys. (2), **6,** p. 467; 1887. Phil. Mag. (5), **25,** p. 425; 1888. Jour. Russian Phys.-chem. Soc., **34,** p. 155; 1902.

Violle. — The radiation of incandescent bodies. Jl. de Phys. (3), **1,** p. 298; 1892. C. R., **114,** p. 734; **115,** p. 1273, 1892. — Radiation from refractory bodies heated in the electric furnace. C. R., **117,** p. 33; 1893.

St. John. — On the equality of light emissivities at high temperatures, etc. Wied. Ann., **56,** p. 433; 1895.

Kurlbaum. — On the new platinum light unit of the Phys. Tech. Reichsanstalt. Verh. Phys. Ges. (Berlin), **14,** p. 56; 1895.

Larmor. — On the relations of radiation to temperature. Nature, **62,** p. 562; 1900. **63,** p. 216. — Planck's eq. Proc. Roy. Soc., **83,** p. 81; 1909. — Theory. Phil. Mag., **20,** p. 353; 1910.

Guillaume. The laws of radiation and the theory of incandescent mantles. Rev. Gén. des Sci., **12,** pp. 358, 422; 1901.

Wien. — Black-body radiation and the second law of thermodynamics. Berl. Ber., p. 55; 1893. — Temperature and entropy of radiation. Wied. Ann., **52,** p. 132; 1894. — The upper limit of wave lengths in the radiation of solid bodies, etc. Wied Ann., **46,** p. 633; 1893. **52,** p. 150; 1894. — On the partition of energy in the emission spectrum of a black body. Wied. Ann., **58,** p. 662; 1896. — On the theory of radiation from a black body. Ann. der Phys., **3,** p. 530; 1900. Paris Cong. Rpts., **2,** p. 23; 1900.

Wien and Lummer. — Method of demonstrating the radiation law for an absolutely black body. Wied. Ann., **56,** p. 451; 1895.

Beckmann. — Black-body radiation, etc. Thesis, Tübingen, 1898.

Lummer. — On the gray glow and red glow. Wied. Ann., **62,** p. 13; 1897. — Radiation from black bodies. Paris Cong. Rpts., **2,** p. 56; 1900. Arch. Math. Phys. (3), **2,** p. 157; 1901. **3,** p. 261; 1902.

Lummer and Jahnke. — Ann. der Phys., **3,** p. 283; 1900.

Compau. — Radiation laws. Ann. Chim. Phys. (7), **26,** p. 488; 1902.

Lummer and Pringsheim. — The radiation from a black body between 100° and 1300° C. Wied. Ann., **63,** p. 395; 1897. — Distribution of energy in spectrum of black body. Verh. Deutsche Phys. Ges., **1,** pp. 23 and 215; 1899. — Infra-red radiation. Verh. Deutsche Phys. Ges., **2,** p. 163; 1900. — On black radiation. Ann. der Phys., **6,** p. 192; 1901. — The theoretical radiation scale, etc., at 2300° absolute. Verh. Deutsche Phys. Ges. (5), **1,** p. 3; 1903.

Lummer and Kurlbaum. — Electrically treated black body and its temperature measurement. Verh. Phys. Ges. (Berlin), **17,** p. 106; 1898. Ann. der Phys., **5,** p. 829; 1901. — On the change of photometric intensity with temperature. Verh. Deutsche Phys. Ges., **2,** p. 89; 1900.

Pringsheim. — Deduction of Kirchhoff's law. Verh. Deutsche Phys. Ges., **3,** p. 81; 1901. — Emission from gases. Paris Cong. Rpts., **2,** 1900.

Bottomley. — Radiation from solids. Phil. Mag. (6), **4,** p. 560; 1902.

Planck. — Entropy and temperature of radiant heat, etc. Ann. der Phys., **1,** p. 719; 1900. Sitzber. Berl. Akad., **1,** p. 440; 1899. — On irreversible radiation. Ann. der Phys., **1,** p. 69; 1900. — On a bettering of Wien's spectral equation. Verh. Deutsche Phys. Ges., **2,** p. 202; 1900. Ann. der Phys., **4,** p. 553; 1901. — Energy distribution in normal spectrum, Verh. D. Phys. Ges., **2,** p. 237; 1900. — Theory. Ann. der Phys., **31,** p. 758; 1910.

Rayleigh. — Phil. Mag. (5), **49,** p. 539; 1900. (6) **1,** p. 98; 1901.

Thiesen. — Verh. Deutsche Phys. Ges., **2,** p. 65; 1900.

Rubens. — Infra-red radiation. Wied. Ann., **69,** p. 576; 1899.

Rubens and E. Nichols. — Wied. Ann., **60,** p. 418; 1897.

Rubens and Kurlbaum. — Experimental verifications. Berl. Ber., p. 929; 1900. Ann. der Phys., **4,** p. 649; 1901. Astrophys. Jl., **14,** p. 335; 1901. Ann. der Phys., **4,** p. 649; 1904.

Maxwell. — Pressure of radiation. Electricity and Magnetism, chap. on Electromagnetic theory.

Bartoli. — Wied. Ann., **22,** p. 31; 1884.

Galitzine. — Wied. Ann., **47,** p. 479; 1892.

Pellat. — Jl. de Phys., July, 1903.

Lebedew. — Ann. de Phys., **6,** p. 433; 1901. Paris Cong. Rpts., **2,** p. 133; 1900.

E. F. Nichols and Hull. — Phys. Rev., 901 and 1903; Astrophys. Jl., **17,** p. 315; 1903.

Rayleigh. — Phil. Mag. (6), **3,** p. 338; 1902.

Day and Van Orstrand. — The black body and the measurement of extreme temperatures. Astrophys. Jl., **19,** p. 1; 1904.

C. Mendenhall and Saunders. — Astrophys. Jl., **13,** p. 25; 1901.

Rasch. — On the photometric determination of temperatures, etc. Ann. der Phys., **13,** p. 193; 1904.

G. W. Stewart. — Spectral-energy curves of black body at room temperature. Phys. Rev., **15,** p. 306; 1902. **17,** p. 476; 1903.

Cotton. — Kirchhoff's Law. Rev. Gén. des Sci., Feb. 15, 1899. Astrophys. Jl., **9,** p. 237; 1899.

Ångström. — Gaseous Absorption. Ann. der Phys., **6,** p. 163; 1901.

Bahr. — Ibid., **29,** p. 780; 1909.

Valentiner. — Stefan's law and gas scale to 1600° C. Ann. der Phys. (4), **31,** p. 275; 1910.

V. Wartenberg. — Emissive powers **vs.** temperature. Verh. Phys. Ges., **12,** p. 121; 1910.

Holborn and Henning. — Emissive powers. Berl. Akad. Ber., p. 311; 1905.

Burgess. — Radiation from Cu. Bull. Bureau Standards, **6,** p. 111; 1909.

Poynting. — Radiation in the Solar System. Phil. Trans., **202,** p. 525; 1903.

Féry. — Ann. Chim. et Phys., **17,** p. 267; 1909. Rev. Gén. d. Sci., Sept., 1903. — Stefan's law. C. R., **148,** pp. 915, 1150; 1909. — Conical Receivers. C. R., **148,** p. 777; 1909. — Selective Receivers. C. R., **148,** p. 1043; 1909.

Nernst. — From Gases. Phys. Zs., **5,** p. 777; 1904.

Holborn and Henning. — Light Emission and Melting Points. Berlin Sitz. Ber., **12,** p. 311; 1905.

Lucas. — Pt Radiation. Phys. Zs., **6,** p. 418; 1905.

Burgess. — Pt Radiation. Bull. Bureau Standards, **1,** p. 443; 1905.

Hertzsprung. — Radiation and Luminous Equivalent. Zs. wiss. Photographie, **4,** p. 42; 1906.

Jeans. — Theory. Proc. Roy. Soc., **76,** p. 545; 1905. Phil. Mag., **12,** p. 57; 1906. **17,** p. 229; 1909.

Lummer and Pringsheim. — Welsbach Mantle. Phys. Zs., **7,** p. 89; 1906. — Lorentz-Jeans Formula. Phys. Zs., **9,** p. 449; 1908.

Swinburne. — Proc. Phys. Soc., **20,** p. 33; 1906. Engineering (Lond.), **82,** p. 217; 1906.

Cantor. — Radiation and Doppler's Principle. Ann. der Phys., **20,** p. 333; 1906.

Thomson (J. J.). — Electrical Origin of Radiation. Phil. Mag., **14,** p. 217; 1907. — Theory. Phil. Mag., **20,** p. 238; 1910.

Lorentz. — Theory. N. Cimento, **16,** p. 5; 1908.

Richardson. — Ionization and Temperature. Phys. Rev., **27,** p. 183; 1908.

Coblentz. — Radiation Constants. Bull. Bureau Standards, **5,** p. 339; 1909. — Reflecting Power of Metals. Jl. Frank. Inst., Sept., 1910.

Hagen and Rubens. — Emissivity and Temperature. Sitz. Berlin Akad., **16,** p. 478; 1909. **23,** p. 467; 1910.

H. A. Wilson. — Theory. Proc. Roy. Soc., **82,** p. 177; 1909. Phil. Mag., **20,** p. 121; 1910.

Pokrovzkij. — Spectrophotometric Relations. Jl. Russ. Phys.-chem. Soc., **41,** p. 73; 1909.

Polara. — Theory. Accad. Lincei, **18,** p. 513; 1909.

Bauer and Moulin. — Stefan's Law. C. R., **149,** p. 988; 1909. C. R., **150,** p. 167; 1910.

Einstein. — Theory. Phys. Zs., **10,** p. 185; 1909.

Saurel. — Theory. Phys. Rev., **30,** p. 350; 1910.

Féry and Drecq. — Stefan's Law. Jl. de Phys. (5), **1,** p. 551; 1911.

Parmentier. — Stefan's Law. Ann. Ch. et Phys., **22,** p. 417; 1911.

Warburg and Leithauser. — Wien's law. Sitz. Berlin Akad., p. 925; 1910. P. T. R. Thätigkeit, 1910.

Humphreys. — Summary. Astrophys. Jl., **31,** p. 281, 1910.

Violle. — Report on Radiation. Ann. Ch. et Phys. (8), **2,** p. 134; 1904.

Drysdale. — Luminous Efficiency of Black Body. Jl. de Phys. (4), **8,** p. 197; 1909.

RADIATION PYROMETER.

Violle. — Solar radiation. Ann. Chim. et Phys. (5), **20,** p. 289; 1877. Jour. de Phys., p. 277; 1876.

Rosetti. — Ann. Chim. et Phys., **17,** p. 177; 1879. Phil. Mag., **18,** p. 324; 1879.

Deprez and d'Arsonval. — Société de Physique, Feb. 5, 1886.

Boys. — Radiomicrometer. Phil. Trans., **180,** p. 159; 1887.

Wilson and Gray. — Temperature of the sun. Phil. Trans., **185,** p. 361; 1894.

Langley. — Bolometer. Am. Jour. Sci., **21,** p. 187; 1881. **31,** p. 1; 1886. **32,** p. 90; 1886. (4), **5,** p. 241; 1898. Jour. de Phys., **9,** p. 59.

Terreschin. — Diss. St. Petersburg, 1898. Jour. Russ. Phys.-chem. Ges., **29,** pp. 22, 169, 277; 1897.

Petavel. — Proc. Roy. Soc., **63,** p. 403; 1898. Phil. Trans., **191,** p. 501; 1898.

Abbot. — Bolometer. Astrophys. Jour., **8,** p. 250; 1898.

Belloc. — Bolometer errors. L'éclair. élec. (5), **15,** p. 383; 1898.

Scheiner. — Radiation and temperature of sun (Leipzig), 1899.

Warburg. — Temperature of sun. Verh. D. Ges. (1), **2,** p. 50; 1899.

Féry. — The measurement of high temperatures and Stefan's law. C. R., **134,** p. 977; 1902. Jl. de Phys., Sept., 1904.

Rubens. — Sensitive Thermopile. Zs. Instr'k., **18,** p. 65; 1898.

Féry. — C. R., **134,** p. 977; 1902. — Spiral Pyrometer. Engineering (Lond.), **87,** p. 663; 1909. Bull. Soc. Franç. Phys., p. 186; 1907.

Coblentz. — Radiation Instruments. Bull. Bureau Standards, **4,** p. 391; 1908.

Foster. — Trans. Am. Electroch. Soc., **17,** p. 223; 1910.

Ångström. — Pyrheliometer. Astrophys. Jl., **9,** p. 232. Solar Research Int. Union, **1,** p. 178.

Callendar. — Absolute Bolometer. Proc. Roy. Soc., **77,** p. 6; 1905. Phys. Soc. Lond., May 12, 1905; July 8, 1910.

Kimball. — Pyrheliometers. Bull. Mt. Weather Obs., **1,** p. 83; 1908.

Abbot and Fowle. — Pyrheliometers and Bolometers. Annals Smithsonian Astrophys. Obs., **2,** 1908.

Abbot. — Silver-disc Pyrheliometer. Smithsonian Misc. Coll., **56,** p. 1; 1911.

Thwing. — Jl. Frank. Inst., May, 1908.

OPTICAL PYROMETER.

See also laws of radiation under Lummer, Pringsheim, Kurlbaum, Wanner, Wien, Rasch, Féry, etc.

Kirchhoff. — Ann. Chim. et Phys., **59,** p. 124; 1860.

Ed. Becquerel. — Optical measurement of temperatures. C. R., **55,** p. 826; 1863. Ann. Chim. et Phys., **68,** p. 49; 1863.

Violle. — Radiation from platinum. C. R., **88,** p. 171; 1879. **91,** pp. 866, 1204; 1881.

Kurlbaum and Schulze. — Pyrometric examination of Nernst lamps. Verh. D. Phys. Ges. (5), **24**, p. 425; 1903.

D. Berthelot. — On a new optical method, etc. Ann. Chim. et Phys. (7), **26**, p. 58; 1902.

Lummer. — Photometric pyrometer. Verh. D. Phys. Ges., p. 131; 1901.

Féry. — Temperature of the arc. C. R., **134**, p. 1201; 1902. — Absorption Pyrometer. Jl. de Phys. (4), **3**, p. 32; 1904.

Le Chatelier Pyrometer. — On the measurement of high temperatures. C. R., **114**, pp. 214–216; 1892. Jl. de Phys. (3), **1**, pp. 185–205; 1892. Industrie électrique, April, 1892. — On the temperature of the sun. C. R., **114**, pp. 737–739; 1892. — On the temperatures of industrial furnaces. C. R., **114**, pp. 470–473; 1892. Introduction to Metallurgy (*Roberts-Austen*), 1903. — Discussion of Le Chatelier's method: (*Violle*) C. R., **114**, p. 734; 1892. Jl. de. Phys. (3), **1**, p. 298; 1892. (*Becquerel*) C. R., **114**, pp. 225 and 390; 1892. (*Le Chatelier*) C. R., **114**, p. 340; 1892. (*Crova*) C. R., **114**, p. 941; 1892. Kayser's Spectroscopy, 1902.

Crova's Pyrometer. — Spectrometric study of certain luminous sources. C. R., **87**, pp. 322–325; 1878. — On the spectrometric measurement of high temperatures. C. R., **87**, pp. 979–981; 1878. — Study of the energy of radiations emitted by calorific and luminous sources. Jour. de Phys., **7**, pp. 357–363, 1878. — Spectrometric measurement of high temperatures. Jour. de Phys.; **9**, pp. 196–198; 1879. C. R., **90**, pp. 252–254; 1880. Ann. Chim. et Phys. (5), **19**, pp. 472–550; 1880. — Photometric comparison of luminous sources of different lines. C. R., **93**, pp. 512–513; 1881. — Solar photometry. C. R., **95**, pp. 1271–1273; 1882.

End of Spectrum Method. — *A. Crova.* Study of the energy of radiations emitted by calorific and luminous sources. Jour. de Phys., **7**, pp. 357–363; 1878. — *W. Hempel.* On the measurement of high temperatures by means of a spectral apparatus. Zs. f. Angewandte Chem., **14**, pp. 237–242; 1901.

Wanner Pyrometer. — *A. König.* A new spectral photometer. Wied. Ann., **53**, p. 785; 1894. — Description of Wanner instrument. Iron Age, Feb. 18, p. 24; 1904. Phys. Zs., **3**, pp. 112–114; 1902. Stahl und Eisen, **22**, pp. 207–211; 1902. Zs. Vereines Deut. Ing., **48**, pp. 160, 161; 1904. — *Wanner.* Photometric measurement of the radiation of black bodies. Ann. der Phys., **5**, pp. 141–155; 1900. — *Martens and Grinbaum.* Improved form of König spectrophotometer. Ann. der Phys., **5**, p. 954; 1903. — *Hase.* Measurements with Wanner pyrometer. Zs. Anorg. Chem., **15**, p. 715; 1902. — *Nernst and Wartenberg.* Verh. Phys. Ges., **8**, p. 146; 1906. — Low-temperature pyrometer. Jl. Gasbel., **50**, p. 1005; 1907.

Holborn and Kurlbaum Pyrometer. — Sitzber. Berlin Akad., June 13, pp. 712–719; 1901. Ann. der Phys., **10**, p. 225; 1902. See also laws of radiation; melting points.

Morse Thermogage. — American Machinist, 1903.

Henning. — Spectral pyrometer. Zs. Instr'kunde, **30**, p. 61; 1910.

Waidner and Burgess. — Arc Temperature. Phys. Rev., **19**, p. 241; 1904. Bull. Bureau Standards, **1**, p. 109; 1904. — Optical Pyrometry. Phys. Rev., **19**, p. 422; 1904. Bull. Bureau Standards, **1**, p. 189; 1905. — Radiation from Pt and Pd. Bull. Bureau Standards, **3**, p. 163; 1907.

Holborn. — Engineering (Lond.), **84,** p. 345; 1907. Brit. Assoc. Rpt., p. 440; 1907.

Nernst. — Photometric. Phys. Zs., **7,** p. 380; 1906.

Holborn and Valentiner. — Optical ***vs.*** Gas to 1600° C. Ann. der Phys. (4), **22,** p. 1; 1907.

Féry. — Vacuum-tube Temperatures. Soc. Franç. Phys., p. 305; 1907. Jl. de Phys., **6,** p. 979; 1907.

Kurlbaum and Schulze. — Ibid. Berichte D. Phys. Ges., 1906.

Pirani. — Phys. Ges. Verh., **12,** pp. 301, 1054; 1910. **13,** p. 19; 1911.

C. E. Mendenhall. — Phys. Rev., **33,** p. 74; 1911.

H. W. Gillett. — Jl. Phys. Chem., **15,** p. 213; 1911.

Thuermel. — Ann. de Phys., **33,** p. 1139; 1910.

Wartenberg. — Metal temperatures. Verh. D. Phys. Ges., **12,** p. 121; 1910.

EXPANSION AND CONTRACTION PYROMETERS.

Wedgwood. — Phil. Trans., **72,** p. 305; 1782. **74,** p. 358; 1784.

Weinhold. — Pogg. Ann., **149,** p. 186; 1873.

Bolz. — Die Pyrometer, Berlin, 1888.

Guyton and Morveau. — Ann. Chim. et Phys., 1st Series, **46,** p. 276; 1803. **73,** p. 254; 1810. **74,** pp. 18, 129; 1810. **90,** pp. 113, 225; 1814.

The Meldometer. — *J. Joly.* Proc. Roy. Irish Academy (3), **2,** p. 38; 1891. — *Ramsay and Eumorfopoulos.* Phil. Mag., **41,** p. 360; 1896.

High-range Mercury Thermometers. — *Weber.* Ber. Berlin Akad., Dec., 1903. *Wiebe,* ibid., July, 1884, Nov., 1885; Zs. Instr'kunde, **6,** p. 167; 1886. **8,** p. 373; 1888. **10,** p. 207; 1890. *Schott,* ibid., **11,** p. 330; 1891. — *Hovestadt.* Jenaer Glas (trans. by J. D. and A. Everett). — *Marchis.* Modifications permanentes du verre, etc. — *Dickinson.* Bull. Bureau of Standards, **2,** p. 189; 1906. — *Guillaume.* Treatise on Thermometry of Precision. (Gauthier Villars, 1889.) — *Fischer and Bobertag.* Glass Therms. for High Temps. Zs. f. Elek. Ch., **14,** p. 375; 1908. — *Bureau of Standards.* Circ., **8,** 2nd Ed., 1911.

Quartz Thermometers. — *Dufour.* C. R., **188,** p. 775; 1900. — *Siebert.* Zs. Elektroch. (Halle), **10,** p. 26.

FUSIBLE-CONE PYROSCOPE.

Lauth and Vogt. — Pyrometric measurements. Bull. Soc. Chim., **46,** p. 786; 1886.

Seger. — Tonindustrie Zeitung, p. 121; 1885. Pp. 135, 229; 1886.

Tonindustrie Zs., No. 49, 1893; No. 52, 1895; No. 119, 1908.

Stahl u. Eisen, p. 440; 1909. P. 1505; 1910.

A. Beranger. — Matériaux et Produits Réfractaires (Paris, 1910). (Very complete account.) Zs. Angew. Chem., p. 49; 1905. Sprechsaal, pp. 118, 156, 391, 483; 1907. P. 1284; 1906. P. 561; 1908.

Rothe. — Tonindustrie Zs., **30,** p. 1473; 1906. **31,** p. 1365; 1907.

Hoffmann. — Tonindustrie Zs., **33,** p. 1577; 1909.

Cramer and Hecht. — Tonindustrie Zs., No. 18, 1896.

Seger's Schriften.

Simonis. — Tonindustrie Zs., **31,** p. 146; 1907. **32,** p. 1764; 1908.

H. O. Hofmann. — Trans. Am. Inst. Mining Eng., **24,** p. 42. Thätigkeit P. T. Reichsanstalt for 1909, 1910.

PYROMETERS BASED ON FLOW OF FLUIDS.

A. Job. — Viscosity pyrometer. C. R., **134,** p. 39; 1902.

Uhling and Steinbart. — Stahl u. Eisen, 1899.

Carnelly and Burton. — Water circulation. Jl. Chem. Soc. (Lond.), **45,** p. 237; 1884. Also described in Sir Roberts-Austen's Metallurgy, 1902.

Barus. — Bull. **54,** Geolog. Survey, 1889.

E. A. Uehling. — Proc. Cleveland Inst. Engrs., Jan., 1900. Electroch. and Met. Ind., **3,** p. 160; 1905.

RECORDING PYROMETERS.

Le Chatelier. — Study of clays. C. R., **104,** p. 144; 1887. — Quenching of Steels. Rev. de Métallurgie, **1,** p. 134; 1904.

Roberts-Austen. — First Report to the Alloys Research Committee. Proc. Inst. Mech. Engrs., p. 543; 1891. Nature, **45,** 1892; B. A. Report, 1891; Jour. of Soc. of Chem. Industry, **46,** p. 1; 1896. Proc. Inst. Mech. Eng., p. 269; 1895. Pp. 67, 243; 1897. Proc. Roy. Soc., **49,** p. 347; 1891. Fifth Report Alloys Research Committee, 1899. Proc. Inst. Mech. Eng., p. 35; 1899. Metallographist, **2,** p. 186; 1899.

G. Charpy. — Study of the hardening of steel. Bull. de la Soc. d'encouragement (4), **10,** p. 666; 1895.

Callendar. — Platinum recording pyrometer. Engineering, May 26, p. 675, 1899. Phil. Mag., **19,** p. 538; 1910.

Stansfield. — Phil. Mag. (5), **46,** p. 59; 1898. Phys. Soc. London (2), **16,** p. 103; 1898.

Bristol. — Air pyrometer. Eng. News, Dec. 13, 1900.

Saladin. — Iron and Steel Metall. and Metallog., **7,** p. 237; 1904.

Queen and Co. — Electroch. and Met. Ind., **3,** p. 162; 1905.

Siemens and Halske. — Zs. Instrumentenk., **24,** p. 350; 1904. **25,** p. 273; 1905.

Einthoven. — Arch. Neerland, **10,** p. 414. Proc. Acad. Sci. Amsterdam (2), **6,** p. 707; 1904.

Benedicks. — Iron and Steel Inst., II, p. 153; 1908.

Le Chatelier. — Rev. de Métallurgie, **1,** p. 134; 1904.

Wologdine. — Rev. d. Métallurgie, **4,** p. 552; 1907.

Kurnakow. — Zs. Anorg. Ch., **42,** p. 184; 1904.

Schmidt. — Chem. Eng., **6,** p. 80; 1907.

Harkhort. — Metallurgie, **4,** p. 639; 1907.

Bristol. — Trans. Am. Inst. Mech. Engrs., **22,** No. 874, p. 143.

Dejean. — Rev. de Métallurgie, **2,** p. 701; 1905. **3,** p. 149; 1906.

Burgess. — Methods of Obtaining Cooling Curves. Bull. Bureau Standards, **5,** p. 199; 1908.

Bruger. — Phys. Zs., p. 775; 1906.

Brown. — Electroch. and Met. Ind., **7,** p. 329; 1909.
Northrup. — Proc. Am. Electroch. Soc., May, 1909.
Rengade. — Bull. Soc. Chim., **7,** p. 934; 1909.
Hayes. — Proc. Am. Acad., **47,** p. 3; 1911.

VARIOUS PYROMETRIC METHODS.

Quincke. — Acoustic Thermometer. Ann. d. Phys., **63,** p. 66; 1897.
Krupp's Hot-blast Pyrometer. — *Von Bergen.* Jl. Iron and Steel Inst., **1,** p. 207; 1886.
A. H. Sexton. — Fuel and Refractory Materials. Chapter on Pyrometry; several industrial forms described.
T. Hurter. — Industrial Air Pyrometer. Jl. Soc. Chem. Ind., p. 634; 1886.
Wiborgh's Pyrometer. — Jl. Iron and Steel Institute, **2,** p. 110; 1880.
Fournier's Vapor Pressure Thermometers. — Engineering (Lond.) **89,** p. 447; 1910.

MELTING POINTS.

METALS.

Prinsep. — Ann. Chim. et Phys. (2), **41,** p. 247; 1829.
Lauth. — Bull. Soc. Chim., Paris, **46,** p. 786; 1886.
E. Becquerel. — Ann. Chim. et Phys. (3), **68,** p. 497; 1863.
Violle. — C. R., **85,** p. 543; 1877. **87,** p. 981; 1878. **89,** p. 702; 1879.
Holborn and Wien. — Wied. Ann., **47,** p. 107; 1892. **56,** p. 360; 1895. Also Zs. für Instr'k., p. 257; 1892.
Holborn and Day. — Ann. d. Phys. (1), **4,** p. 99; 1901. Am. Jour. Sci., **11,** p. 145; 1901. Wied. Ann., **68,** p. 817; 1899. Am. Jour. Sci. (4), **8,** p. 165; 1899.
Ehrhardt and Schertel. — Jahrb. für das Berg- und Hüttenw. im K. Sachsen, p. 154; 1879.
Callendar. — Phil. Mag. (5), **47,** p. 191; 1899. **48,** p. 519.
Curie. — Ann. de Chim. et de Phys. (5), **5,** 1895.
Barus. — Bull. **54,** U. S. Geological Survey, 1889. Behandlung u. Messung hoher Temp. Leipzig, 1892. Am. Jour. Sci. (3), **48,** p. 332; 1894.
Berthelot. — C. R., **126,** Feb., 1898.
Le Chatelier. — C. R., **114,** p. 470; 1892.
Moldenke. — Zs. für Instr'k., **19,** p. 153; 1898. (Iron and steel.)
Cusack. — Proc. Roy. Irish Acad. (3), **4,** p. 399; 1899.
Landolt and Börnstein. — Phys. Chem. Tabellen, Berlin.
Carnelly. — Melting and Boiling Point Tables, London, 1885.
Smithsonian Physical Tables, 5th ed., 1910. .
Holman, Lawrence, and Barr. — Phil. Mag. (5), **42,** p. 37; 1896. Proc. Am. Acad., **31,** p. 218.
Heycock and Neville. — Phil. Trans., **189,** p. 25. Jour. Chem. Soc., **71,** p. 333; 1897. Nature, **55,** p. 502; 1897. Chem. News, **75,** p. 160; 1897.
Heræus. — Manganese. Zs. Elecktroch., **8,** p. 185; 1902.
Nernst. — Zs. Elektrotech., 1903.

Rasch. — Ann. d. Phys., 1904.

D. Berthelot. — Ann. Chim. et Phys., 1902. — Gold. C. R., **138,** p. 1153; 1904.

Richards. — Application of phase rule to Cu, Ag, Au. Am. Jl. Sci. (4), **13,** p. 377; 1902.

Jaquerod and Perrot. — Gold. C. R., **138,** p. 1032; 1904.

Pirani and Meyer. — Ta. Verh. D. Phys. Ges., **13,** p. 540; 1911.

Féry and Cheneveau. — Pt. C. R., **148,** p. 401; 1909.

Carpenter. — Iron. Iron and Steel Inst. III., p. 290; 1908.

Lewis. — Cr. Chem. News, **86,** p. 13; 1902.

Holborn and Henning. — Sn, Cd, Zn. Ann. d. Phys., **35,** p. 761; 1911.

Day and Allen. — Phys. Rev., **19,** p. 177; 1904.

Day and Clement. — Am. Jl. Soc., **26,** p. 405; 1908.

Day and Sosman. — Zn to Pd. Am. Jl. Sci., **29,** p. 93; 1910.

Tammann and Associates in Zs. Anorg. Chem. Metals and Binary Alloys.

Tammann. — Pressure influence on Sn and Bi. Zs. Anorg. Ch., **40,** p. 54; 1904.

Johnston and Adams. — Ibid. Amer. Jl. Sci., **31,** p. 501; 1911.

Arndt. — Review. Verein. z. Beförd. d. Gewerbefleisses, Verhandt., p. 265; 1904.

Harker. — Pt and Ni. Proc. Roy. Soc., **76,** p. 235; 1905.

Nernst and Wartenberg. — Pd and Pt. Phys. Ges. Verh., **8,** p. 48; 1906.

Holborn and Valentiner. — Pd and Pt. Sitzber. Berlin Akad., **44,** p. 811; 1906.

Waidner and Burgess. — Pd and Pt. Bull. Bureau Standards, **3,** p. 163; 1907. — Pt. C. R., May 3, 1909. — W and Ta. Jl. d. Phys., **6,** p. 830; 1907. — Reproducibility of Metal M.P.'s. Bull. Bureau Standards, **6,** p. 149; 1909.

Burgess. — Iron Group. Bull. Bureau Standards, **3,** p. 345; 1907. — Chemical Elements. Jl. Wash. Acad. Sci., **1,** p. 16; 1911.

Dejean. — Copper. Rev. d. Métallurgie, **3,** p. 149; 1906.

Mendenhall and Ingersoll. — Pd, Rh, Ir on Nernst Glower. Phys. Rev., **25,** p. 1; 1907.

Locke. — A wire method. Zs. Elektroch., **13,** p. 592; 1907.

Wartenberg. — W. Chem. Ber., **40,** p. 3287; 1907. — Refractory Metals. Phys. Ges. Verh., **12,** p. 121; 1910.

Ruff. — Refractory Metals and Oxides. Chem. Ber., **43,** p. 1564; 1910.

Bolton. — Niobium. Zs. Elek. Ch., **13,** p. 145; 1907.

SALTS AND MISCELLANEOUS.

Carnelly. — J. C. S. Trans., p. 489; 1876. P. 365; 1877. P. 273; 1878.

Le Chatelier. — Bull. Soc. Chim., **47,** p. 301. C. R., **118,** pp. 350, 711, 802.

V. Meyer, Riddle, and Lamb. — Ch. Ber., **27,** p. 3129; 1894.

MacCrae. — Ann. d. Phys., **55,** p. 95; 1894.

Hütner and Tammann. — Zs. Anorg. Ch., **43,** p. 215; 1905.

Ruff and Plato. — Ch. Ber., **36,** p. 2357; 1903.

Joly. — Proc. Irish Acad., No. 2, 1891.

Ramsay and Eurmorfopoulos. — Phil. Mag., **41,** p. 360; 1896.

Day and Sosman. — Am. Jl. Sci., **31,** p. 341; 1911.

Grenet. — Rev. de Métallurgie, **7,** p. 485; 1910.

Brearly and Morewood. — Sentinel Pyrometers. Jl. Iron and Steel Inst., **73,** p. 261; 1907.

Liebknecht and Nilsen. — Ch. Ber., **36,** p. 3718; 1903.

Watson. — Phys. Rev., **26,** p. 198; 1908.

C. H. Burgess and A. Holt. — Rapid for borates, etc. Proc. Roy. Sci. Lond., Nov. 24, 1904.

W. C. Heræus. — Ceramics. Zs. Angew. Chem., p. 49; 1905.

Doelter. — Silicates. Zs. Elektroch., **12,** p. 617; 1906.

Lampen. — Porcelains, etc. Jl. Am. Ch. Soc., **28,** p. 846; 1906.

White. — Thermoelectric manipulation. Am. Jl. Sci., **28,** p. 453; 1909.

Boudouard. — Slags. Jl. Iron and Steel Inst. (1), **67,** p. 350; 1905.

BOILING POINTS.

Barus. — (*See* Melting Points.) Am. Jour. Sci. (5), **48,** p. 332; 1894.

Troost. — C. R., **94,** p. 788; 1882. **94,** p. 1508; 1882. **95,** p. 30; 1882.

Le Chatelier. — C. R., **121,** p. 323; 1895. (*See also under* Thermoelectric Pyrometer.)

Berthelot. — Séances de la soc. de physique, Paris, Feb., 1898, and Bull. du Muséum, No. 6, p. 301; 1898.

Callendar and Griffiths. — Proc. Roy. Soc. London, **49,** p. 56; 1891.

Chappuis and Harker. — Travaux et Mém. du Bureau Int. des Poids et Mesures, **12,** 1900; Phil. Trans., 1900.

Preyer and V. Meyer. — Zeits. für Anorg. Chem., **2,** p. 1; 1892. Berl. Ber., **25,** p. 622; 1892.

S. Young. — Trans. Chem. Soc., p. 629; 1891.

MacCrae. — Wied. Ann., **55,** p. 95; 1895.

Callendar. — Phil. Mag. (5), **48,** p. 519; 1899. (Fusion also.)

D. Berthelot. — Ann. Chim. et Phys., 1902.

Féry. — Cu and Zn. Ann. Chim. et Phys. (7), **28,** p. 428; 1903.

R. Rothe. — Sulphur. Zs. Instrumk., **23,** p. 364; 1903.

Greenwood. — Of metals. Proc. Roy. Soc., **A 82,** p. 396; 1909. **83,** p. 483; 1910. Chem. News, **104,** pp. 31, 42; 1911.

Kraft and Merz. — S, Se, Te at reduced pressure. Chem. Ber., **36,** p. 4344; 1903.

Ruff and Johannsen. — Alkali metals. Chem. Ber., **38,** p. 3601; 1905.

Harker and Sexton. — Pressure change of S.B.P. Elect. Rev., **63,** p. 416; 1908.

Eumorfopoulos. — Sulphur. Proc. Roy. Soc., **81,** p. 339; 1908.

Callendar and Moss. — Sulphur. Proc. Roy. Soc., **83,** p. 106; 1909.

Holborn and Henning. — Sulphur, etc. Ann. d. Phys. (4), **35,** p. 761; 1911.

Waidner and Burgess. — Sulphur. Bull. Bureau Standards, **7,** p. 127; 1911.

Wartenberg. — Metals. Zs. Anorg. Chem., **56,** p. 320; 1908.

Moissan. — Metals. Ann. Ch. et Phys. (8), **8,** p. 145; 1906.

Watts. — Metals. Trans. Am. Electroch. Soc., **12,** p. 141; 1907.

Smith and Menzies. — Hg. Jl. Am. Ch. Soc., **32,** p. 1434; 1910.

Jaquerod and Wassmer. — Benzophenone and Naphthaline. Jl. d. Ch. et de Phys., **2,** p. 52; 1904.

Waidner and Burgess. — Ibid. Bull. Bureau Standards, **7,** p. 3; 1910.

PYROMETRIC MATERIALS.

PORCELAIN: EXPANSION.

Deville and Troost. — C. R., **57,** p. 867; 1863.
Bedford. — B. A. Report, 1899.
Benoît. — Trav. et Mém. du Bureau Int., **6,** p. 190.
Tutton. — Phil. Mag. (6), **3,** p. 631; 1902.
Chappuis. — Phil. Mag. (6), **3,** p. 243; 1902.
Holborn and Day. — Ann. der Phys. (4), **2,** p. 505; 1900.
Holborn and Gruniesen. — Ann. der Phys. (4), **6,** p. 136; 1901.

METALS: EXPANSION.

Holborn and Day. — Ann. der Phys., **4,** p. 104; 1901. Am. Jl. Sci. (4), **11,** p. 374; 1901.
Le Chatelier. — C. R., **128,** p. 1444; 1899. **129,** p. 331. **107,** p. 862; 1888. **108,** p. 1046; 1896. **111,** p. 123; 1890.
Charpy and Grenet. — C. R., **134,** p. 540; 1902.
Terneden. — Thesis, Rotterdam, 1901 (Fortsch. der Phys., 1901).
Dittenberger. — Zs. Ver. Deutsche Ingen., **46,** p. 1532; 1902.
Day and Sosman. — Am. Jl. Sci., **29,** p. 111; 1910.

QUARTZ.

Le Chatelier. — C. R., **107,** p. 862; 1888. **108,** p. 1046; **111,** p. 123; **130,** p. 1703.
Callendar. — Chem. News, **83,** p. 151; 1901.
Holborn and Henning. — Ann. der Phys., **4,** p. 446; 1903.
Scheel. — Deutsch. Phys. Ges. (5), **5,** p. 119; 1903. — Verh. Phys. Tech. Reichsanstalt, 1904.
Shenstone. — Properties of Amorphous Quartz. Nature, **64,** pp. 65 and 126; 1901. Contains history to date.
Dufour. — Tin-quartz thermometer. C. R., **130,** p. 775.
Villard. — Permeability for H at 1000° C. C. R., **130,** p. 1752.
Joly. — Plasticity, etc. Nature, **64,** p. 102; 1901.
Moissan and Siemens. — Action of water on. C. R., **138,** p. 939; 1904. — Solubility in Zn and Pb. C. R., **138,** p. 86; 1904. — Vapor pressure of. C. R., **138,** p. 243; 1904.
Heræus. — Properties: a general summary. Zs. Elektroch., **9,** p. 848; 1903.
Brun. — Fusion. Arch. Sc. Phys. Nat. (Geneva) (4), **13,** p. 313; 1902.
Hutton. — Lamps, etc. Am. Electroch. Soc., Sept., 1903.
Day and Shepherd. — Science, **23,** p. 670; 1906.

GLASS: EXPANSION.

Holborn and Gruniesen. — Ann. der Phys. (4), **6,** p. 136; 1901.
Bottomley and Evans. — Phil. Mag., **1,** p. 125; 1901.
Hovestadt. — Jenaer Glas.

REFRACTORIES.

(*See also* Furnaces.)

E. K. Scott. — Furnace linings. Faraday Soc., 1905. Electroch. and Met. Ind., **3**, p. 140; 1905.

A. Beranger. — Matériaux et Produits Réfractaires (Paris, 1910).

Neumann. — Stahl u. Eisen, **30**, p. 1505; 1910. (Bibliography of alumina-lime-silica.)

Fitzgerald. — Furnace materials. Electroch. Ind., **2**, p. 439, 490; 1904.

Dunn. — Soc. Ch. Ind. Jl., **23**, p. 1132; 1904.

Brauner. — Bibliography of Clays and the Ceramic Arts. American Ceramic Society.

Hutton and Beard. — Conductivity. Faraday Soc. Trans., **1**, p. 264; 1905.

Wologdine. — Conductivity, etc. Bull. Soc. d'Encour., **8**, p. 879; 1909.

Schoen. — Use of Quartz Tubes. Metallurgie, **5**, p. 635; 1908.

Walden. — Jl. Am. Ch. Soc., **30**, p. 1351; 1908.

Acheson. — Siloxicon. Electroch. Ind., **6**, p. 379; 1908.

Arndt. — Berlin Magnesia. Chem. Ztg., **30**, p. 211; 1906.

Goodwin and Mailey. — Phys. Rev., **23**, p. 22; 1906.

Aubrey. — Bauxite. Electroch. and Met. Ind., **4**, p. 52; 1906.

Bleninger. — Fire Clays. Proc. Eng. Soc. West. Penn., **25**, p. 565; 1910.

Bywater. — Jl. of Gas Lighting, **102**, p. 831; 1908.

Bölling. — Silundum. Electroch. Ind., **7**, p. 24; 1909.

Tucker. — Ibid., **7**, p. 512; 1909.

Buchner. — Fused Alumina. Zs. Anorg. Ch., **17**, p. 985; 1904.

Phalen. — Alundum. Electroch. Ind., **7**, p. 458; 1909.

Day and Shepherd. — Lime-silica. Am. Jl. Sci., **22**, p. 265; 1906.

Shepherd and Rankine. — Binary Systems. Am. Jl. Sci., **28**, p. 293; 1909.

Heinicke. — Magnesia-alumina. Zs. Anorg. Ch., **21**, p. 687; 1908.

Iddings. — Igneous Rocks. 1909. (Wiley & Sons.)

Moissan. — Le Four Electrique. (Also in English.)

Sexton. — Fuel and Refractory Materials.

VARIOUS SUBJECTS.

Le Chatelier. — Specific heat of carbon. C. R., **116**, p. 1051; 1893. Soc. Franç. de Phys., No. 107, p. 3; 1898.

Barus. — Bull. of U. S. Geological Survey No. 54, 1889. (Pyrometry.) Report on the progress of pyrometry to the Paris Congress, 1900. — Viscosity and temperature. Wied. Ann., **96**, p. 358; 1899. *Callendar.* — Nature, **49**, p. 494; 1899. — Long-range temperature and pressure variables in physics. Nature, **56**, p. 528; 1897.

Baly and Chorley. — Liquid-expansion pyrometer. Berl. Ber., **27**, p. 470; 1894.

Dufour. — Tin in quartz pyrometer. C. R., **180**, p. 775; 1900.

Berthelot. — Interference method of high-temperature measurements. C. R., **120**, p. 831; 1895. Jour. de Phys. (3), **4**, p. 357; 1895. C. R., Jan., 1898; applications in C. R., Feb., 1898.

Moissan. — Le Four Electrique, Paris, 1898. (Also in English.)

Töpler. — Pressure-level apparatus. Wied. Ann., **56,** p. 609; 1895. **57,** p. 311; 1896.

Quincke. — An acoustic thermometer for high and low temperatures. Wied. Ann., **63,** p. 66; 1897.

K. Scheel. — Ueber Fernthermometer. Verlag v. C. Marhold, Halle, 1898. 48 pp.

Heitmann. — Ueber einen neuen Temperatur-Fernmessapparat von Hartmann und Braun. E. T. Z., **19,** p. 355; 1898.

Chree. — Recent work in thermometry. Nature, **58,** p. 304; 1898.

Lêmeray. — On a relation between the dilation and the fusing points of simple metals. C. R., **131,** p. 1291; 1900.

Holborn and Austin. — Disintegration of the platinum metals in different gases. Phil. Mag. (6), **7,** p. 388; 1904.

Stewart. — (Same as preceding.) Phil. Mag. (5), **48,** p. 481; 1899.

Hagen and Rubens. — On some relations between optical and electrical properties of metals. Phil. Mag. (6), **7,** p. 157; 1904.

Kahlbaum. — On the distillation of metals. Phys. Zs., p. 32; 1900.

Kahlbaum, Roth, and Seidler. — Ibid. Zs. Anorg. Ch., **29,** p. 177; 1902.

Glaser. — Latent and sp. hts. of metals. Métallurgie, **1,** pp. 103, 121; 1904.

Richards. — Metallurgical calculations.

Scudder. — Liquid baths for melting-point determinations. Chem. News, **88,** p. 104; 1903.

Guertler. — Devitrification temperatures. Zs. Anorg. Ch., **40,** p. 268; 1904.

Kraft and Bergfeld. — Lowest evaporation temperatures of metals in vacuo. Chem. Ber., **38,** p. 254; 1905.

Kraft. — Boiling metals in vacuo. Chem. Ber., **38,** p. 262; 1905.

Wiebe. — Melting Points *vs.* Expansion. Phys. Ges. Verh., **8,** p. 91; 1906.

J. W. Richards. — Latent Heat of Vaporization, Metals, etc. Am. Electroch. Soc. Trans., **13,** p. 447; 1908.

F. C. Mason. — Magnetic Pyrometer. Am. Machinist, **33,** p. 875.

Pawlow. — Melting *vs.* Surface Tension. Zs. Phys. Ch., **65,** p. 1; 1908.

Hot-blast pyrometers. *Roberts-Austen's* Metallurgy. J. Iron and Steel Inst., pp. 195, 240; 1884. P. 235; 1885. P. 207; 1886. **2,** p. 110; 1888. Proc. Inst. M. E., p. 53; 1852. Jl. Soc. Chem. Ind., p. 40; 1885. P. 16; 1897.

Wiborgh. — Industrial Air Pyrometer. Jl. Ir. and St. Inst., **2,** p. 110; 1888.

Callendar. — Industrial Air Pyrometer. Proc. Roy. Soc., **50,** p. 247; 1892. — Measurement of extreme temperatures. Nature, **59,** pp. 495 and 519 — a review of various pyrometric methods.

Siebert. — Quartz Thermometers. Zs. Elektroch. (Halle), **10,** p. 26.

Mahlke. — On a comparison apparatus for thermometers between 250° and 600° C. Zs. Instr'kunde, **14,** p. 73; 1894.

F. Kraft. — Evaporation and boiling of metals in quartz in electric furnace. Ber. Deut. Ch. Ges., **36,** p. 1690; 1903.

CHEMICAL DETERMINATIONS OF TEMPERATURES.

Haber and Richardt. — The water-gas equilibrium in the Bunsen flame, and the chemical determination of high temperatures. Zs. Anorg. Chem., **38,** p. 5; 1904.

Zenghelis. — Chemical reactions at very high temperatures. Zs. Phys. Chem., **46,** p. 287; 1903.

Nernst. — On the determination of high temperatures. Phys. Zs., **4,** p. 733; 1903.

THERMOCHEMICAL DATA.

Haber. — Technical Gas Reactions, 1908. (Tr. by A. B. Lamb.)

Nernst. — $Q = RT^2 (d \log K/dT)$. Phys. Zs., **4,** p. 733; 1903.

Haber and Associates. — Gas Combustion Phenomena. Zs. Phys. Chem., **68,** p. 726. **69,** p. 337; 1909. **71,** p. 29; 1910.

Zenghelis. — Zs. Phys. Chem., **46,** p. 287; 1903.

Wartenberg. — Reviews. Fortschritte d. Chemie, **2,** p. 205; 1910.

V. Jüptner. — Energy relations. Zs. Anorg. Ch., **42,** p. 235; 1904.

Wartenberg. — Phys. Ges. Verh., **8,** p. 97; 1906.

Nernst and Wartenberg. — H_2O and CO_2 dissociation. Zs. Phys. Chem., **56,** pp. 513, 534, 548; 1906.

Tucker and Lampen. — Carborundum Formation Temperatures. Jl. Am. Chem. Soc., **28,** p. 853; 1906.

Hutton and Petavel. — High-temperature Electrochemistry. (References.) Electrician, **50,** pp. 308, 349; 1902. Phil. Trans., **207,** p. 421; 1908.

INCANDESCENT-LAMP TEMPERATURES.

Le Chatelier. — Jl. d. Phys. (6), **1,** p. 203; 1892.

Lummer and Pringsheim. — Verh. D. Phys. Ges., **1,** pp. 23, 215; 1899.

Janet. — C. R., **123,** p. 690; 1896. **123,** p. 734; 1898.

Pirani. — Verh. Phys. Ges., **12,** p. 301; 1910.

Féry and Chéneveau. — C. R., **149,** p. 777; 1909. Jl. de Phys., **9,** p. 397; 1910.

Waidner and Burgess. — Bull. Bureau Standards, **2,** p. 319; 1907. Elec. Wld. **48,** p. 915; 1906.

Henning. — Zs. Instr'kunde, **30,** p. 61; 1910.

Grau. — Elektrotech. u. Maschinenb., **25,** p. 295; 1907.

Coblentz. — Bull. Bureau Standards, **5,** p. 339; 1908.

Morris, Stroud, and Ellis. — Electrician, **59,** pp. 584, 624; 1907.

Jolley. — Electrician, **63,** pp. 700, 755; 1909.

TEMPERATURE OF FLAMES.

Kurlbaum. — Phys. Zs., **3,** p. 187; 1902.

Lummer and Pringsheim. — Phys. Zs., **3,** p. 233; 1902.

E W. Stewart. — Phys. Rev., 1902, 1903.

Féry. — C. R., **137,** p. 909; 1903.

Haber and Richardt. — Zs. Anorg. Chem., **38,** p. 5; 1904.

Haber and Hodsman. — Zs. Phys. Chem., **67,** p. 343; 1909.

Becker. — Ann. der Phys., **28,** p. 1017; 1909.

Allner. — Jl. für Gasbelencht., **48,** pp. 1035, 1057, 1081, 1107; 1905.

Amerio. — Accad. Sci. Torino, **41,** p. 290; 1905.

Ladenburg. — Phys. Zs., **7,** p. 697; 1906.

Schmidt. — Phys. Ges. Verh., **11,** p. 87; 1909.

Shea. — Bunsen with Thermocouples. Phys. Rev., **30,** p. 397; 1910.

E. Bauer. — Le Radium. Dec. 6, 1909. C. R., **147,** p. 1397; 1908. C. R., **148,** pp. 908, 1756; 1909.

SOLAR AND STELLAR TEMPERATURES.

(*See also* Radiation Pyrometer.)

Abbot. — The Sun, 1911. Astro. phys. Jl. **34,** p. 197; 1911.

Pringsheim. — Physik der Sonne, 1910.

Goldhammer. — Ann. d. Phys., **25,** p. 905; 1908.

Millochau. — C. R., **148,** p. 780; 1909. Jl. de Phys., **8,** p. 347; 1909.

Wilsing and Scheiner. — Pub. Astrophys. Obs., Potsdam, No. 56, **19.** Astrophys. Jl., **32,** 130; 1910.

Abbot and Fowle. — Pub. Astrophys. Obs. Smithsonian Institution, **2,** 1908. Astrophys. Jl., **29,** p. 281; 1909.

Nordmann. — C. R., **149,** pp. 557, 662, 1038; 1909. **150,** pp. 448, 669; 1910. Bull. Astron., Apr., 1909, p. 170.

Kurlbaum. — Sitzber. Berlin Akad., **25,** p. 541; 1911.

LABORATORY FURNACES.

A. Kalähne. — On electric resistance furnaces. Ann. d. Phys., **11,** p. 257; 1903.

E. Haagen. — Platinum-foil furnaces. Zs. Elektroch., p. 509; 1902.

W. C. Heræus. — Electrical laboratory furnace. Zs. Elektroch., p. 201; 1902. Electrician, **49,** p. 519. **50,** p. 173; 1902.

C. L. Norton. — Laboratory electric furnaces. Elec. World and Eng., **36,** p. 951; 1900.

F. A. J. Fitzgerald. — Principles of resistance furnaces. Trans. Am. Elec. Chem. Soc., **4,** p. 9; Elec. chem. Indus., **2,** p. 242; 1904.

D. Berthelot. — Ann. Phys. et Chim., **26,** p. 58; 1902.

Holborn and Day. — Ann. der Phys., **2,** p. 505; 1900.

Doelter. — Electric furnaces for melting points. Centralbl. f. Min., p. 426; 1902.

Day and Allen. — Phys. Rev., **19,** p. 177; 1904.

King. — Carbon vacuum tube. Astrophys. Jl., **28,** p. 300; 1908.

Tucker. — Tube furnace. Tr. Am. Electroch. Soc., **11,** p. 303; 1907.

Lampen. — Jl. Am. Ch. Soc., **28,** p. 846.

Stansfield. — The Electric Furnace (McGraw-Hill Co.).

H. Moisan. — Le Four Electrique. (Also in English.)

J. Wright. — Electric Furnaces and Their Application. (Henley Pub. Co.)

Hutton and Petavel. — Inst. Elec. Eng. (Manchester Sec.), Nov. 25, 1902. Jl. of, **32,** p. 227; 1903.

Hutton and Patterson. — Electroch. and Met. Ind., p. 455; 1905. Trans. Faraday Soc., **1,** p. 187.

Hutton. — Electrician, **58,** p. 579; 1907.

Howe. — Electric muffle. Proc. Am. Soc. Test. Materials, **6,** p. 202; 1906.

Friedrich. — Gas metallographic furnace. Metallurgie, **3,** p. 206; 1906. — Electric furnaces, Metallurgie, **4,** p. 778; 1907. Jl. Am. Ch. Soc., **28,** p. 921; 1906.

Arsem. — Vacuum Furnace. Jl. Am. Chem. Soc., **28,** p. 921; 1906. Trans. Am. Electroch. Soc., **9,** p. 153; 1906. Jour. Eng. Chem., Jan., 1910.

Ruff. — Vacuum Furnace. Ch. Ber., **43,** p. 1564; 1910.

V. Wartenberg. — Tungsten furnace. Zs. Elek. Ch., **15,** p. 876; 1909.

Heræus. — Iridium Furnace. Zs. Angew. Chem., **18,** p. 49; 1905.

Of Kriptol: Zs. Angew. Chem., **18,** p. 239; 1905. Metallurgie, **4,** pp. 617, 778; 1907. **5,** pp. 186, 638; 1908.

Müller. — Vacuum Furnace. Metallurgie, **6,** p. 145; 1909.

Oberhoffer. — Vacuum Furnace. Metallurgie, **4,** p. 427; 1907.

Sabersky-Adler. — Electric hardening furnace. Trans. Faraday Soc., **5,** p. 15; 1909.

Harker. — Solid Electrolyte Tube. Proc. Roy. Soc., **76,** p. 235; 1905.

THERMOSTATS AND FURNACE CONTROL.

H. Darwin. — Electric Thermostat. Electrician, **52,** p. 256. Astrophysical Jl., **20,** p. 347; 1904.

Morris, Ellis, and Stroud. — Automatic Rheostat Control. Electrician (Lond.), **61,** p. 400; 1908.

Sodeau. — Regulators. Soc. Chem. Ind. Jl., **23,** p. 1134; 1904.

Plato. — Mechanical automatic rheostat. Zs. Phys. Ch., **55,** p. 721; 1906.

Portevin. — Continuous water rheostat. Rev. de Métallurgie, **5,** p. 295; 1908.

Kolowrat. — Electro-optical regulator. Jl. d. Phys., **8,** p. 495; 1909.

Bodenstein. — Thermostats. Faraday Soc., May 23, 1911.

METALLOGRAPHIC PRACTICE.

Frankenheim. — Cooling curves. Pogg. Ann., **39,** p. 376; 1836.

Plato. — Cooling Curves. Zs. Phys. Ch., **55,** p. 721; 1906. **58,** p. 350; 1908. **63,** p. 447.

Osmond. — Cooling Curves. C. R., **103,** pp. 743, 1112; 1886. **104,** p. 985; 1887. Annales des Mines, **14,** p. 1; 1888.

Wüst. — Cooling Curves. Metallurgie, **3,** p. 1; 1906.

Tammann. — Thermal analysis. Zs. Anorg. Chem., **37,** p. 303; 1903. **45,** p. 24, 1905. **47,** p. 289; 1905.

Portevin. — Thermal analysis. Rev. de Métallurgie, **4,** p. 979; 1907. **5,** p. 295; 1908.

Dejean. — Cooling Cúrves. Rev. de Métallurgie, **2,** p. 701; 1905. **3,** p. 149; 1906.

Le Chatelier. — Microscopic Methods. Rev. de Métallurgie, **3,** p. 359; 1906.

Robin. — Hardness of Steels at High Temperatures. Rev. de Métallurgie, **5,** p. 893; 1908.

W. Rosenhain. — Observations on Recalescence Curves. Phys. Soc. Lond., **21,** p. 180; 1908. Proc. Inst. of Metals.

G. K. Burgess. — On Methods of Obtaining Cooling Curves. Electroch. and Met. Ind., **6,** pp. 366, 403; 1908. Bull. Bureau Standards, **5,** p. 199; 1908.

Guertler. — Treatise on Métallographie, 1909.

Oberhoffer. — Metallographic Examination in Vacuo at High Temperatures. Metallurgie, **6,** p. 554; 1909.

Heyn. — Progress from 1906 to 1909. Rev. de Métallurgie, **7,** p. 34; 1910. (With bibliography.)

Ruer. — Treatise on Metallography, 1907.

Shepherd. — Thermometric Analysis of Solid Phases. Jl. Phys. Chem., **8,** p. 92; 1904.

Desch. — Metallography, 1910. (Longman.)

Guillet. — Traitements Thermiques, 1909. (Dunod.)

Cavalier. — Alliages Métalliques, 1909.

Carpenter and Keeling. — Steels. Jl. Iron and Steel Inst., p. 224; 1904.

SPECIFIC HEAT.

Iron: P. Oberhoffer. Metallurgie, **4,** pp. 447, 486; 1907. — Weiss and Beck, Jl. d. Phys., **7,** p. 255; 1908. Harker. Phil. Mag., **10,** p. 430; 1905. — *And Nickel:* Lecher. Phys. Ges. Verh., **9,** p. 647; 1907.

Carbon: Kunz. Ann. d. Phys., **14** p. 309; 1904.

Gases: Pier. Zs. Elektroch., **15,** p. 536; 1909. — Holborn and Austin. Berlin Sitz. Ber., **5,** p. 175; 1905. — Holborn and Henning. Ann. d. Phys., **23,** p. 809; 1907.

Metals: Stücker. Wien. Sitz. Ber., **114,** p. 657; 1905. — Tilden. Phil. Trans. **194,** p. 233; 1900. **201,** p. 37; 1903. table of sp hts [illegible]

Steam: Holborn and Henning. Ann. d. Phys., **18,** p. 739; 1905.

Iron-carbon: Oberhoffer and Meuthen. Metallurgie, **5,** p. 173; 1908. — Byström. Fortschritte d. Phys., **16,** p. 369; 1860.

Silicates and Pt: White. Am. Jl. Sci., **28,** p. 334; 1909.

Platinum: Plato. Zs. Phys. Ch., **55,** p. 736; 1906. — Violle. C. R., **85,** p. 543; 1877.

Copper: Naccari. Atti. di Torino, **23,** p. 107; 1887. — Richards and Frazier. Chem. News, **68,** 1893. — Le Verrier. C. R., **114,** p. 907; 1892.

Ferromagnetic substances: Dumas. Arch. Sci. Phys. Nat., **29,** pp. 352, 458; 1910.

NH_3 and chemical equilibrium. Nernst. Zs. Elek. Ch., **16,** p. 96; 1910.

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TABLE I.—TEMPERATURE CONVERSION TABLE.

(Dr. L. Waldo, in *Metallurgical and Chemical Engineering*, March, 1910.)

C	**0**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**
	F	**F**	**F**	**F**	**F**	**F**	**F**	**F**	**F**	**F**
−200	−328	−346	−364	−382	−400	−418	−436	−454	......	......
−100	−148	−166	−184	**−202**	−220	−238	−256	−274	−292	**−310**
− 0	+ 32	+ 14	− 4	− 22	− 40	− 58	− 76	− 94	**−112**	−130
0	32	50	68	86	**104**	122	140	158	176	194
100	**212**	230	248	266	284	**302**	320	338	356	374
200	392	**410**	428	446	464	482	**500**	518	536	554
300	572	590	**608**	626	644	662	680	698	**716**	734
400	752	770	788	**806**	824	842	860	878	896	**914**
500	932	950	968	986	**1004**	1022	1040	1058	1076	1094
600	**1112**	1130	1148	1166	1184	**1202**	1220	1238	1256	1274
700	1292	**1310**	1328	1346	1364	1382	**1400**	1418	1436	1454
800	1472	1490	**1508**	1526	1544	1562	1580	1598	**1616**	1634
900	1652	1670	1688	**1706**	1724	1742	1760	1778	1796	**1814**
1000	1832	1850	1868	1886	**1904**	1922	1940	1958	1976	1994
1100	**2012**	2030	2048	2066	2084	**2102**	2120	2138	2156	2174
1200	2192	**2210**	2228	2246	2264	2282	**2300**	2318	2336	2354
1300	2372	2390	**2408**	2426	2444	2462	2480	2498	**2516**	2534
1400	2552	2570	2588	**2606**	2624	2642	2660	2678	2696	**2714**
1500	2732	2750	2768	2786	**2804**	2822	2840	2858	2876	2894
1600	**2912**	2930	2948	2966	2984	**3002**	3020	3038	3056	3074
1700	3092	**3110**	3128	3146	3164	3182	**3200**	3218	3236	3254
1800	3272	3290	**3308**	3326	3344	3362	3380	3398	**3416**	3434
1900	3452	3470	3488	**3506**	3524	3542	3560	3578	3596	**3614**
2000	3632	3650	3668	3686	**3704**	3722	3740	3758	3776	3794
2100	**3812**	3830	3848	3866	3884	**3902**	3920	3938	3956	3974
2200	3992	**4010**	4028	4046	4064	4082	**4100**	4118	4136	4154
2300	4172	4190	**4208**	4226	4244	4262	4280	4298	**4316**	4334
2400	4352	4370	4388	**4406**	4424	4442	4460	4478	4496	**4514**
2500	4532	4550	4568	4586	**4604**	4622	4640	4658	4676	4694
2600	**4712**	4730	4748	4766	4784	**4802**	4820	4838	4856	4874
2700	4892	**4910**	4928	4946	4964	4982	**5000**	5018	5036	5054
2800	5072	5090	**5108**	5126	5144	5162	5180	5198	**5216**	5234
2900	5252	5270	5288	**5306**	5324	5342	5360	5378	5396	**5414**
3000	5432	5450	5468	5486	**5504**	5522	5540	5558	5576	5594
3100	**5612**	5630	5648	5666	5684	**5702**	5720	5738	5756	5774
3200	5792	**5810**	5828	5846	5864	5882	**5900**	5918	5936	5954
3300	5972	5990	**6008**	6026	6044	6062	6080	6098	**6116**	6134
3400	6152	6170	6188	**6206**	6224	6242	6260	6278	6296	**6314**
3500	6332	6350	6368	6386	**6404**	6422	6440	6458	6476	6494
3600	**6512**	6530	6548	6566	6584	**6602**	6620	6638	6656	6674
3700	6692	**6710**	6728	6646	6764	6782	**6800**	6818	6836	6854
3800	6872	6890	**6908**	6926	6944	6962	6980	6998	**7016**	7034
3900	7052	7070	7088	**7106**	7124	7142	7160	7178	7196	**7214**
C	**0**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**

C°	**F°**
1	1.8
2	3.6
3	5.4
4	7.2
5	9.0
6	10.8
7	12.6
8	14.4
9	16.2
10	18.0

F°	**C°**
1	0.56
2	1.11
3	1.67
4	2.22
5	2.78
6	3.33
7	3.89
8	4.44
9	5.00
10	5.56
11	6.11
12	6.67
13	7.22
14	7.78
15	8.33
16	8.89
17	9.44
18	10.00

Examples. 1347° C. = 2444° F. + 12.6° F. = 2456.6° F.; 3367° F. = 1850° C. + 2.78° C. = 1852.78° C.

TABLE II.—MELTING POINTS (C.) OF THE CHEMICAL ELEMENTS.*

(Standard Temperatures are in small capitals.)

Element.	Melting point.	Remarks.
Helium	< −269?	B. P. He = −268.5. Kamerlingh-Onnes.
Hydrogen	−259	Travers-Jaquerod.
Neon	−253?	
Oxygen	−230?	Range −227 to −235.
Fluorine	−223	Moissan-Dewar.
Nitrogen	−210.5	Fischer-Alt.
Argon	−188	Ramsay-Travers.
Krypton	−169	Ramsay-Travers.
Xenon	−140	Ramsay-Travers.
Chlorine	−101.5	Johnson-McIntosh.
MERCURY	−38.7±0.5	
Bromine	−7.3	Range −7.5 to −7.0.
Cæsium	26	Range 25.3 to 26.5.
Gallium	30.1	Lecoq-Boisbaudran.
Rubidium	38	Range 37.8 to 38.5.
Phosphorus	44.1	Hulett.
POTASSIUM	62.3±0.2	
Sodium	97.5±1.0	
Iodine	114±1	
Sulphur	113.5 to 119.5	Various forms.
Indium	154.5±0.5	
Lithium	186	Kahlbaum.
Selenium	217 to 220	Various forms. Saunders.
TIN	231.9±0.2	
Bismuth	270	Range 267.5 to 271.5.
Thallium	302±1	
CADMIUM	321.0±0.2	Range 320.0 to 321.7.
LEAD	327.4±0.4	
ZINC	419.4±0.3	Range 418.2 to 419.4.
Tellurium	451±1	
Arsenic	500? 850	Guntz-Broniewski. Jolibois.
ANTIMONY	630±1	"Kahlbaum" purity only.
Cerium	635	
Magnesium	650±2	
ALUMINIUM	658±1	
Calcium	805±5	
Lanthanum	810?	Muthmann-Weiss.
Strontium	>Ca, <Ba?	
Neodymium	840?	Muthmann-Weiss.
Barium	850	Guntz.
Germanium	<Ag	Winkler.
Praseodymium	940?	Muthmann-Weiss.
SILVER	961±2	
Radium	600 to 1200?	Unknown.
GOLD	1063±3	

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* G. K. Burgess, *Jl. Wash. Acad. Sci.*, **1**, p. 16, 1911.

MELTING POINTS (C.) OF THE CHEMICAL ELEMENTS. (*Cont'd.*)

Element.	Melting point.	Remarks.
COPPER	1083 ± 3	
Manganese	1225 ± 15	
Yttrium	1000 to 1400?	Unknown.
Samarium	1300 to 1400	Muthmann-Weiss.
Scandium	1000 to 1400?	Unknown.
Silicon	1420 ± 15	
NICKEL	1450 ± 10	Day-Sosman = 1452.
Cobalt	1490	Day-Sosman.
Chromium	1505 ± 15	
IRON	1520 ± 15	
PALLADIUM	1550 ± 15	Day-Sosman = 1549.
Zirconium	> Silicon	Troost.
Thorium	> 1700, < Pt	Wartenberg.
Vanadium	1730 ± 30	
PLATINUM	1755 ± 20	Waidner-Burgess = 1753.
Beryllium	> 1800	Parsons.
Ytterbium	1600 to 2000?	Unknown.
Titanium	2200 to 2400?	Weiss-Kaiser.
	1800 to 1850	Hunter.
Rhodium	1920?	Range 1907 to 1970.
Ruthenium	> 1950	Joly.
Niobium	2200?	v. Bolton = 1950.
Boron	2200 to 2500	Weintraub.
Iridium	2300?	Range 2100 to 2350.
Uranium	near Mo	Moissan.
Molybdenum	2500?	Range 2110 to > 2500.
Osmium	2700?	Waidner-Burgess.
Tantalum	2850	Waidner-Burgess = 2910.
TUNGSTEN	3000 ± 100	Range 2575 to 3250. Waidner-Burgess = 3080.
Carbon	?	Unknown.

TABLE III.—BOILING POINT OF WATER.

Temperature Centigrade; Barometer in mm. of Mercury.

mm.	0	1	2	3	4	5	6	7	8	9
730	98.880	98.918	98.956	98.994	99.032	99.069	99.107	99.145	99.183	99.220
740	99.258	99.295	99.333	99.370	99.407	99.445	99.482	99.519	99.557	99.594
750	99.631	99.668	99.705	99.742	99.779	99.816	99.853	99.890	99.926	99.963
760	100.000	100.037	100.073	100.110	100.146	100.183	100.219	100.256	100.292	100.327

TABLE IV.—BOILING POINT OF SULPHUR.

Temperature Centigrade; Barometer in mm. of Mercury.

mm.	0	1	2	3	4	5	6	7	8	9
730	442.00	442.09	442.18	442.27	442.36	442.45	442.53	442.62	442.71	442.80
740	442.89	442.98	443.07	443.16	443.25	443.34	443.43	443.52	443.61	443.70
750	443.79	443.88	443.97	444.06	444.15	444.24	444.34	444.43	444.52	444.61
760	**444.70**	444.79	444.88	444.97	445.06	445.15	445.25	445.34	445.43	445.52

This table is based on the assumption that the normal boiling point of sulphur is 444.70. The other temperatures are computed by Holborn and Henning's formula.

TABLE V.—RESISTANCE THERMOMETER SCALE (CENTIGRADE).

Values of Temperature Centigrade (*t*) in Terms of Platinum Temperatures (*pt*) for Thermometers with $\delta = 1.500$.

pt	*t*	Difference for 1° *pt*.	*pt*	*t*	Difference for 1° *pt*.	*pt*	*t*	Difference for 1° *pt*.	*pt*	*t*	Difference for 1° *pt*.
0	0.000	0.985	**250**	255.99	1.066	**500**	534.89	1.170	**750**	844.26	1.313
10	9.867	0.988	260	266.67	1.070	510	546.62	1.175	760	857.42	1.319
20	19.762	0.991	270	277.38	1.073	520	558.40	1.180	770	870.65	1.326
30	29.687	0.994	280	288.13	1.077	530	570.22	1.185	780	883.95	1.333
40	39.641	0.997	290	298.92	1.081	540	582.10	1.190	790	897.32	1.340
50	49.625	1.000	**300**	309.75	1.084	**550**	594.03	1.195	**800**	910.76	1.347
60	59.639	1.003	310	320.61	1.088	560	606.00	1.200	810	924.28	1.355
70	69.683	1.006	320	331.51	1.092	570	618.03	1.205	820	937.87	1.363
80	79.758	1.009	330	342.46	1.096	580	630.11	1.210	830	951.54	1.370
90	89.863	1.012	340	353.44	1.100	590	642.24	1.216	840	965.28	1.378
100	100.00	1.015	**350**	364.46	1.104	**600**	654.43	1.222	**850**	979.10	1.386
110	110.17	1.018	360	375.52	1.108	610	666.67	1.227	860	993.01	1.394
120	120.37	1.021	370	386.62	1.112	620	678.97	1.232	870	1007.00	1.403
130	130.60	1.024	380	397.76	1.116	630	691.32	1.238	880	1021.07	1.411
140	140.86	1.027	390	408.95	1.120	640	703.73	1.244	890	1035.23	1.420
150	151.16	1.031	**400**	420.18	1.125	**650**	716.20	1.250	**900**	1049.47	1.428
160	161.49	1.034	410	431.45	1.129	660	728.73	1.256	910	1063.80	1.437
170	171.85	1.038	420	442.77	1.134	670	741.32	1.261	920	1078.21	1.445
180	182.25	1.041	430	454.13	1.138	680	753.97	1.267	930	1092.71	1.455
190	192.68	1.044	440	465.53	1.142	690	766.67	1.274	940	1107.31	1.464
200	203.14	1.048	**450**	476.97	1.146	**700**	779.44	1.280	**950**	1122.00	1.474
210	213.64	1.052	460	488.46	1.151	710	792.27	1.286	960	1136.79	1.484
220	224.18	1.055	470	500.00	1.156	720	805.17	1.293	970	1151.69	1.494
230	234.75	1.058	480	511.58	1.160	730	818.13	1.299	980	1166.68	1.503
240	245.35	1.062	490	523.21	1.165	740	831.16	1.306	990	1181.76	1.513
250	255.99	1.066	**500**	534.89	1.170	**750**	844.26	1.313	**1000**	1196.95	1.524

TABLE VI.—RESISTANCE THERMOMETER SCALE (FAHR.).

$\delta = 1.50.$

Platinum temperatures.	Gas scale temperatures.	Platinum temperatures.	Gas scale temperatures.	Platinum temperatures.	Gas scale temperatures.	Platinum temperatures.	Gas scale temperatures.
0	0.56	510	522.7	1040	1122.8	1570	1805.5
10	10.35	520	533.4	1050	1134.8	1580	1819.4
20	20.19	530	544.2	1060	1146.9	1590	1833.4
30	30.03	540	554.9	1070	1158.9	**1600**	**1847.4**
32	32.0	550	565.7	1080	1171.0	1610	1861.6
40	39.9	560	576.5	1090	1183.1	1620	1875.6
50	49.8	570	587.3	**1100**	**1195.3**	1630	1889.9
60	59.7	580	598.2	1110	1207.5	1640	1904.1
70	69.5	590	609.1	1120	1219.7	1650	1918.3
80	79.5	**600**	**620.0**	1130	1232.0	1660	1932.5
90	89.4	610	630.9	1140	1244.3	1670	1946.8
100	**99.4**	620	641.8	1150	1256.6	1680	1961.2
110	109.3	630	652.8	1160	1270.0	1690	1975.7
120	119.3	640	663.8	1170	1281.3	**1700**	**1990.2**
130	129.3	650	674.8	1180	1293.7	1710	2004.7
140	139.4	660	685.8	1190	1306.1	1720	2019.3
150	149.4	670	696.9	**1200**	**1318.7**	1730	2034.0
160	159.4	680	707.9	1210	1331.1	1740	2048.7
170	169.5	690	719.0	1220	1343.7	1750	2063.4
180	179.6	**700**	**730.1**	1230	1356.3	1760	2078.2
190	189.7	710	741.3	1240	1368.9	1770	2093.1
200	**199.8**	720	752.5	1250	1381.5	1780	2108.0
210	209.9	730	763.6	1260	1394.2	1790	2123.0
212	212.0	740	774.8	1270	1406.9	**1800**	**2138.0**
220	220.1	750	786.0	1280	1419.6	1810	2153.1
230	230.3	760	797.3	1290	1432.4	1820	2168.3
240	240.5	770	808.6	**1300**	**1445.2**	1830	2183.5
250	250.7	780	819.9	1310	1458.1	1840	2198.7
260	260.9	790	831.2	1320	1471.0	1850	2213.0
270	271.2	**800**	**842.6**	1330	1483.9	1860	2229.4
280	281.4	810	854.0	1340	1496.8	1870	2244.9
290	291.7	820	865.4	1350	1509.8	1880	2260.4
300	**302.0**	830	876.8	1360	1522.9	1890	2276.0
310	312.3	840	888.3	1370	1535.9	**1900**	**2291.6**
320	322.7	850	899.7	1380	1549.1	1910	2307.3
330	333.0	860	911.2	1390	1562.1	1920	2323.0
340	343.4	870	922.7	**1400**	**1575.3**	1930	2338.9
350	353.8	880	934.3	1410	1588.5	1940	2354.8
360	364.2	890	945.9	1420	1601.8	1950	2370.8
370	374.6	**900**	**957.5**	1430	1615.1	1960	2386.8
380	385.1	910	969.1	1440	1628.4	1970	2402.9
390	395.6	920	980.8	1450	1641.8	1980	2419.0
400	**406.1**	930	992.5	1460	1655.2	1990	2435.3
410	416.6	940	1004.2	1470	1668.7	**2000**	**2451.6**
420	427.1	950	1015.9	1480	1682.2	2010	2468.0
430	437.6	960	1027.7	1490	1695.7	2020	2484.4
440	448.2	970	1039.5	**1500**	**1709.3**	2030	2500.8
450	458.8	980	1051.3	1510	1722.9	2040	2517.5
460	469.4	990	1063.1	1520	1736.6	2050	2534.2
470	480.0	**1000**	**1075.0**	1530	1750.3	2060	2551.0
480	490.6	1010	1086.9	1540	1764.0	....	....
490	501.3	1020	1098.8	1550	1777.8	....	....
500	**512.0**	1030	1110.8	1560	1791.6	....	....

TABLE VII. — AUXILIARY TO TABLES V AND VI.

Corrections to t for small changes in δ.

Centigrade scale.				Fahrenheit scale.			
	Δt for $\Delta\delta = 0.01$.		Δt for $\Delta\delta = 0.01$.		Δt for $\Delta\delta = 0.01$.		Δt for $\Delta\delta = 0.01$.
50	−0.002	550	+0.247	100	−0.003	1100	+0.53
100	.000	600	.300	200	.000	1200	.64
150	+ .008	650	.357	300	+ .014	1300	.76
200	.020	700	.420	400	.038	1400	.90
250	.037	750	.487	500	.07	1500	1.05
300	.060	800	.560	600	.11	1600	1.23
350	.087	850	.637	700	.18	1700	1.38
400	.120	900	.720	800	.25	1800	1.56
450	.157	950	.807	900	.33	1900	1.73
500	.200	1000	.900	1000	.42	2000	1.95

Computations of t from pt are made by Table V, as if the thermometer had $\delta = 1.50$. The above corrections (Δt) are then applied to the computed values of t for the value of δ proper to the thermometer.

Example. Let $pt = 470.00$, whence $t = 500.00°$ C. by Table V. If $\delta = 1.52$, the corrected value of t is 500.40° C. by Table VII.

TABLE VIII. — TEMPERATURE CORRECTIONS FOR PLATINUM OF DIFFERENT δ.

[Thermometer calibrated by Callendar method, ice, steam, and S. B. P.]

Temperature ° C.	Correction in ° C. for values of δ given below.							
	1.525	1.550	1.575	1.600	1.650	1.700	1.800	1.900
200	+0.02	+0.05	+ 0.08	+ 0.10	+ 0.14	+ 0.16	+ 0.20	+ 0.21
300	+ .02	+ .05	+ .08	+ .11	+ .19	+ .27	+ .45	+ .55
400	.00	.00	+ .01	+ .03	+ .08	+ .14	+ .29	+ .37
500	− .02	− .05	− .09	− .11	− .18	− .24	− .39	− .57
600	− .09	− .18	− .30	− .40	− .62	− .88	− 1.42	− 1.96
700	− .33	− .70	− 1.03	− 1.32	− 1.78	− 2.2	− 2.9	− 3.5
800	− .90	−1.65	− 2.24	− 2.7	− 3.6	− 4.4	− 5.8	− 7.1
900	−1.90	−3.1	− 4.0	− 4.9	− 6.5	− 8.1	−10.8	−13.5
1000	−3.3	−5.2	− 6.8	− 8.2	−10.7	−13.1	−17.1	−20.8
1100	−5.5	−8.1	−10.3	−12.2	−15.7	−18.7	−24.3	−29.1

The above table applies only when the value of δ is that given by using the S. B. P. as third calibration point of a resistance thermometer.

TABLE IX.—TRANSFORMATION TABLE FOR ABSORPTION COEFFICIENTS.

Values of A' corresponding to c' from values of A corresponding to c.

c/c' A	14,200 to 14,300	14,200 to 14,400	14,200 to 14,500	14,200 to 14,600	14,200 to 14,700	14,300 to 14,400	14,300 to 14,500	14,300 to 14,600	14,300 to 14,700	14,400 to 14,500	14,400 to 14,600	14,400 to 14,700	14,500 to 14,600	14,500 to 14,700	14,600 to 14,700
.05	.049	.049	.048	.048	.047	.049	.049	.048	.048	.049	.049	.048	.049	.049	.049
.1	.098	.097	.095	.094	.092	.098	.097	.095	.094	.098	.097	.095	.098	.097	.098
.2	.19	.19	.19	.18	.18	.19	.19	.19	.18	.19	.19	.19	.19	.19	.19
.3	.29	.29	.28	.27	.27	.29	.29	.28	.27	.29	.29	.28	.29	.29	.29
.4	.39	.38	.37	.36	.35	.39	.38	.37	.36	.39	.38	.37	.39	.38	.39
.5	.49	.48	.46	.45	.44	.49	.48	.46	.45	.49	.48	.46	.49	.48	.49
.6	.59	.57	.54	.53	.52	.59	.57	.54	.53	.59	.57	.54	.59	.57	.59
.7	.68	.66	.64	.62	.60	.68	.66	.64	.62	.68	.66	.64	.68	.66	.68
.8	.77	.75	.73	.70	.69	.77	.75	.73	.70	.77	.75	.73	.77	.75	.77
.9	.87	.84	.82	.79	.77	.87	.84	.82	.79	.87	.84	.82	.87	.84	.87

Table based on equation: $c/c' \log A = \log A'$, for use with Wien's law, p. 251, to reduce observations to common value of c_2.

Example. An observer has taken $c_2 = 14{,}200$ in Eq. III, p. 251; it is desired to reduce his results to $c_2 = 14{,}500$. If A observed was 0.50 the corrected value of A' is 0.46 from the table.

TABLE X.—ABSORBING POWERS* FOR POLISHED METALS AND OTHER SUBSTANCES.

Substance. \ Values of λ.	Blue, 0.4	Green, 0.5	Orange, 0.6	Red, 0.7	Infra red.		
					2.0	5.0	8.0
Silver	0.16	0.10	0.075	0.058	0.021	0.015	0.012
Gold	.72	.53	.156	.077	.032	.030	.020
Platinum	.52	.42	.36	.31	.19	.07	.05
Palladium	......	.42	.36	.31	......	......	......
Rhodium	......	.24	.23	.21	.09	.07	.06
Iridium	......	.25	.25	.24	.14	.06	.05
Iron	.50	.45	.42	.41	.22	.09	.06
Copper:							
Liquid	......	.35	.20	.15	......	......	......
Solid	......	.47	.17	.09	......	......	......
Nickel	.47	.39	.35	.31	.17	.06	.05
Tungsten	.53	.51	.49	.46	.15	.06	.04
Tantalum	......	.62	.55	.45	.10	.07	.06
Molybdenum	.56	.55	.52	.50	.18	.08	.06
Chromium	......	.45	.45	.44	.37	.19	.11
Vanadium	......	.44	.43	.42	.32	.18	.10
Antimony	......	......	.47	......	.40	......	......
Magnesium	......	.28	.27	......	.23	.14	.07
Tellurium	......	.52	.52	.52	.49	.41	.28
Silicon	......	.66	.68	.70	.72	.72	.72
Graphite:							
Polished	.79	.78	.77	.76	.65	.50	.45
Matt	......	......	> .90	> .90	......	......	......
Cuprous oxide	......	.70	.70	.65	......	.60	......
Iron oxide	......	......	.65 to .90		......	......	......
Chromium oxide	......	> .90	> .90	> .90	......	......	......
Porcelain	......	......	.25 to .50		......	......	......
Thoria (pure)	......	......	.07 to .13		......	......	......
Alumina	......	......	.10	.10	......	......	......
Zirconia	......	......	.06 to .09		......	......	......
Magnesia	......	......	.06 to .09		......	......	......
Lime	......	......	.10 to .40		......	......	......

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* The absorbing power a = emissive power $e = 1 - r$, where r = reflecting power.

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